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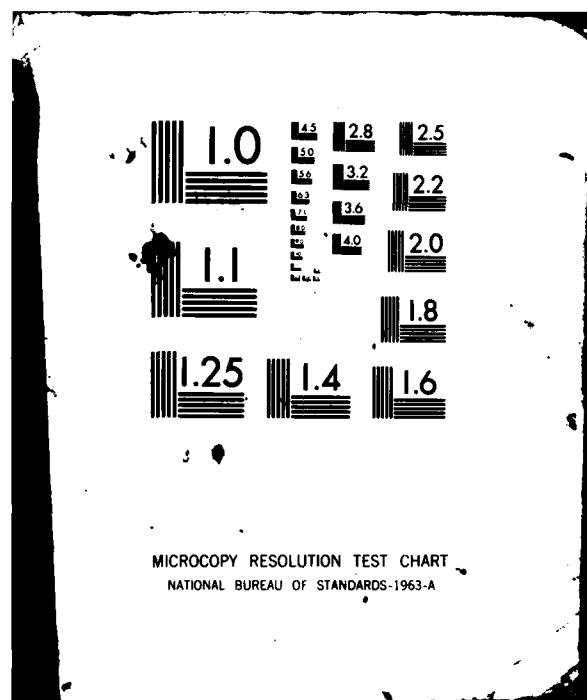
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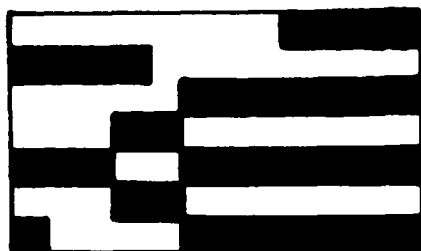
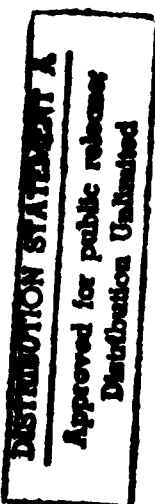
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PHASE TRANSITIONS ON SURFACES

An International Conference
ABSTRACTS AND PROGRAM
3-7 August 1981

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Department of Physics and Astronomy
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Orono, Maine 04469

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The International Conference on Phase Transitions on Surfaces was held at the University of Maine at Orono during the period 3-7 Aug 81. In attendance were a total of 155 scientists from the United States, Europe and Japan. The Program included 18 invited talks, approximately 80 contributed papers and two poster sessions.		

PROGRAM
and
ABSTRACTS
for the
International Conference on
PHASE TRANSITIONS ON SURFACES

August 3-7, 1981
University of Maine at Orono
Orono, Maine 04469

P. Kleban
W. N. Unertl
Co-Chairmen

Funded by:

Xerox Corporation
The Stauffer Chemical Company
The Office of Naval Research
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FOREWORD

The central theme of the international conference on Phase Transitions on Surfaces is phase transitions in two dimensions and equilibrium properties of surface systems. A secondary theme is the relationship of these topics to other areas of surface and interface science and technology and to statistical mechanics.

A principal motivation for this conference is to promote closer communication between the various research communities involved in studies of surface phase behavior, statistical mechanics in two dimensions and related topics. In spite of overlapping interests, such communication has not always been fully developed, partly because of the large volume of research and partly because of the 'natural' division of the subject into various sub-fields such as physisorption and chemisorption. Furthermore, the knowledge gained from studies of phase transitions has important applications in many diverse areas of science and technology. These range from universality in phase transitions and quark confinement to epitaxial growth, heterogeneous catalysis and electrode behavior in electrochemical processes. The potential for scientific advances is obvious. We hope these abstracts reflect a significant part of the intellectual excitement as well as the scientific content of the meeting.

P. Kleban
W. N. Unertl
Co-Chairmen, Phase Transitions
on Surfaces
August 1981

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GENERAL PROGRAM

2 August, Sunday

08:00-18:00	Trip to Acadia National Park and Bar Harbor
18:00-19:00	Dinner, Hilltop Dining Complex
19:00-24:00	Preconference Reception and Registration at Hilltop Dining Complex

3 August, Monday

Session A

101 English-Math

Chairman: A. N. Berker

08:00-08:45	Registration, Lobby, English-Math Building
08:45-09:00	Welcoming Remarks, UMO Vice-President for Academic Affairs, F. E. Hutchinson
09:00-10:30	J. Cahn, "Thermodynamic Properties of Surfaces and Interfaces"
10:30-11:00	Coffee Break
11:00-12:30	R. B. Griffiths, "Statistical Mechanics of Two Dimensional Systems, Part I"
12:30-13:30	Lunch, Hilltop Dining Complex

Session B

Chairman: D. A. King

14:00-15:30	R. L. Park, "Experimental Studies of Two-Dimensional Phase Transitions in Chemisorption Systems"
15:30-16:00	Coffee Break
16:00-17:30	J. G. Dash, "Experimental Studies of Two Dimensional Phase Transitions in Physisorption Systems"
18:00-19:30	Dinner, Hilltop Dining Complex
19:30-23:00	Social Hour, Hilltop Dining Complex
20:00-	Vermere String Quartet Hauck Auditorium (\$3.00 ticket required)

4 August, Tuesday
Session C

101 English-Math

09:00-10:00

10:00-10:20

10:20-11:20

12:30-13:30

Chairman: A. Ignatiev

**D. P. Landau, "Statistical Mechanics of
2d Systems - Models and Calculations"**

Coffee Break

**L. W. Bruch, "Theory of Adatom-Adatom
Interactions in Physisorption Systems"**

Lunch, Hilltop Dining Complex

Session D

14:00-15:00

15:00-15:20

15:20-16:20

18:00-19:30

19:30-23:00

Chairman, H. Van Hove

**T. L. Einstein, "Theory of Adatom-Adatom
Interactions in Chemisorption Systems"**

Coffee Break

**P. Estrup, S. C. Ying and L. Roelofs,
"Phase Transitions on W and Mo Surfaces"**

Dinner, Hilltop Dining Complex

Social Hour, Hilltop Dining Complex

5 August, Wednesday

Session E

101 English-Math

09:00-10:00

10:00-10:20

10:20-11:20

11:40-12:05

12:05-12:30

12:30-12:55

13:00-14:00

14:00-15:00

Chairman: T. L. Einstein

D. A. King, "Surface Diffusion"

Coffee Break

**L. D. Schmidt, "Surface Reactions With
Multiple Surface Phases"**

**J. C. Hamilton and T. Jach, "Phase Transi-
tions on Nickel Single Crystal Surfaces
at the Curie Temperature"**

**P. Kleban, "Chemisorption on Stepped Sur-
faces and Adatom Binding Energies"**

**P. Heiney, et al., "Synchrotron X-ray Study
of Monolayer Xenon Melting"**

Lunch, Hilltop Dining Complex

Free Time for Informal Discussion

Session F - Posters
English-Math Lobby &
101 English-Math

15:00-17:00

17:00-18:00

18:00-19:00

19:00-21:00

21:00-

Chairman: W. N. Unertl

Poster Viewing, Coffee Available

Open Discussion of Posters.

Discussion Leaders: P. Estrup,
L. D. Schmidt and R. L. Park.

Cocktail Hour (open bar). Hilltop
Dining Complex

Lobster Banquet

Maine Humor

6 August, Thursday
Session G
101 English-Math

09:00-10:00

10:00-10:20

10:20-11:20

11:30-12:45

13:00-14:00

14:00-18:00

18:00-19:00

Chairman, J. Zollweg

C. L. Cleveland, "Surface Molecular
Dynamics of Crystallization"

Coffee Break

J. K. Sass, "Electrode-Electrolyte
Interfaces"

Workshop on Metal Surface Reconstructions.
100 English-Math Building.

Lunch, Hilltop Dining Complex

Free Time for Informal Discussion.

Dinner, Hilltop Dining Complex

Session H - Posters
English-Math Lobby

19:00-21:00

21:00-22:00

Chairman, W. N. Unertl

Poster Viewing, Refreshments Available.

Open Discussion of Posters. Discussion

Leaders: C. L. Cleveland, P. H. Kleban,
T. H. Rhodin.

7 August, Friday
Session I

09:00-10:00

Chairman: J. Suzanne

A. H. Berker, "Restructuring and Rescaling:
Adlayer Transitions in Terms of Potts
Lattice Gases, Helical Potts Models, etc.

7 August, Friday
Session 1 (con't.)

10:00-10:20

10:20-11:20

11:40-12:40

12:40-14:00

19:00

Coffee Break

B. I. Halperin, "Theory of the Commensurate Incommensurate Transition"

A. G. Naumovets, "Long-Range Interactions in Alkali Films"

Lunch

Leave on Trip to Baxter State Park to Climb Mt. Katahdin.

8 August, Saturday

22:00

Return from Baxter Trip.

STUDENT SCHOLARSHIP RECIPIENTS

R. D. Diehl	University of Washington
F. M. Ellis	University of Massachusetts
D. A. Huse	Cornell University
R. J. Muirhead	University of Washington
T. W. Root	University of Minnesota
C. Rottman	University of Illinois
K. Shinjo	University of Tokyo
C. Tiby	Joh. Gutenberg-Universität Mainz
K. Ulrich von Raben	Yale University
E. D. Williams	California Institute of Technology

ABSTRACTS OF PAPERS

SESSION A

Monday, August 3

08:00 - 12:30

English-Math 101

A. N. Berker, Chairman

Thermodynamic Properties of Surfaces and Interfaces.
J. W. Cahn

Statistical Mechanics of Two Dimensional Systems, Part I.
R. B. Griffiths

Thermodynamic Properties of Surfaces and Interfaces

John W. Cahn
National Bureau of Standards
Center for Materials Science
Bldg. 223, Rm. A153
Washington, D.C. 20234

Abstract

The classical thermodynamics of fluid films and interfaces will be reviewed. The definition of surfaces excess quantities will be shown to arise naturally from equations, such as the Gibbs adsorption equation, that relate measurable quantities. Phase transitions of interfaces are then described in terms of the singularities of thermodynamic properties.

Conditions for the stability of interfaces, films, and junctions of interfaces will be developed and related to certain kinds of phase transitions. Some important applications of the phase rule and phase diagrams for interfaces will be given.

Solid surface thermodynamics must take into account two important additional factors, anisotropy and a surface stress that differs from surface free energy. Some of the differences will be illustrated by the solid surface version of the Gibbs adsorption equation, shapes of equilibrated solid surfaces, altered stability conditions and some additional phase transitions.

Statistical Mechanics of Two Dimensional Systems, Part I.

Robert B. Griffiths

Physics Department, Carnegie-Mellon University, Pittsburgh, PA 15213

This lecture will present an elementary introduction to the structure and statistical description of crystal surfaces and adsorbed layers on such surfaces. Particular emphasis will be placed on the symmetry of surface phases and the changes in symmetry which occur during phase transitions. The use of phase diagrams for surface phases will be discussed. Finally, there will be a rapid overview of various types of statistical mechanical models used to obtain insight into the nature of two-dimensional phase transitions.

SESSION B

Monday, August 3

14:00 - 17:30

English-Math 101

D. A. King, Chairman

Experimental Studies of Two-Dimensional Phase Transitions in Chemisorption Systems.

R. L. Park

Experimental Studies of Two Dimensional Phase Transitions in Physisorption Systems.

J. G. Dash

EXPERIMENTAL STUDIES OF TWO-DIMENSIONAL PHASE TRANSITIONS
IN CHEMISORPTION SYSTEMS

Robert L. Park
Department of Physics and Astronomy
University of Maryland
College Park, Maryland 20742

One of the most significant generalizations to emerge from low-energy electron diffraction (LEED) studies of single-crystal surfaces is that chemisorbed gas atoms tend to form ordered two-dimensional structures that are simply related to the substrate structure. Thus, chemisorbed atoms are strongly localized on specific sites and should provide a direct experimental test of statistical mechanical theories of two-dimensional lattice gas systems.

Thus far, however, the overwhelming majority of LEED studies have been concerned with the determination of the positions of the adsorbed atoms in the 2-D unit mesh, relative to the substrate atoms. For this purpose, LEED analysis makes use only of the positions and total intensities of diffraction spots, which involves the implicit assumption that the structure repeats itself endlessly and flawlessly. At finite temperatures, however, long-range order can be lost through the formation of antiphase boundaries, which manifest themselves in the broadening of the diffraction spots.

The largely kinematic origin of the spot profiles will be discussed in terms of elementary diffraction theory involving the pair-correlation function of the adsorbed structure, modified by instrumental effects. The application of this analysis to the determination of the critical exponents [1] for the order-disorder transition of oxygen atoms in the $p(2 \times 2)$ structure on (111) nickel will be discussed in detail, and the results compared to recent predictions of lattice gas theories. The extent to which comparison with theory is limited by the finite coherence of the LEED system and the perfection of the substrate surface will also be discussed.

[1] L. D. Roelofs, A. R. Kortan, T. L. Einstein and R. L. Park, Phys. Rev. Lett. 46, 1465 (1981).

Experimental Studies of Two Dimensional Phase Transitions in Physisorption Systems*

J. G. Dash, University of Washington, Seattle, WA 98195

Physically adsorbed monolayer films can approximate certain models of two dimensional matter. The most stringent tests of a model are often obtained from examinations of phase transitions. Variations of thermodynamic quantities with coverage and temperature indicate whether transitions are first order or continuous. In the critical regions of second order transitions critical exponents reveal the basic symmetries of film-substrate structure.

Current experimental studies are now subjecting theories of films to searching examinations. Several striking examples of close correlation between theory and experiment have been obtained. Among these are a number of first order phase transitions, observed by a variety of techniques: solid-vapor, liquid-vapor, and solid-hypercritical fluid condensation, and triple point melting. Notable examples of second order phase changes are the order-disorder transitions of He on graphite and on Kr-plated graphite and the registered solid-fluid transition of Kr on graphite, which have critical exponents in striking agreement with theoretical values.

There are also several classes of transitions with conflicting results, between different experimental techniques or between experiments and conventional models. These include many cases of presumed liquid-vapor coexistence, two-phase melting, and commensurate-incommensurate transitions. In some cases the discrepancies may indicate the need for substantial revision of models. In others the difficulty lies in the inadequate characterization of substrate heterogeneity. Improved substrates and more sophisticated models incorporating heterogeneity are required. These requirements will probably become increasingly important as long as interest in phase transitions continues.

* Supported by National Science Foundation, Grant DMR 78 22697.

SESSION C

Tuesday, August 4

09:00 - 11:20

English-Math 101

A. Ignatiev, Chairman

Statistical Mechanics of 2d Systems - Models and Calculations
D. P. Landau

Theory of Adatom-Adatom Interactions in Physisorption Systems
L. W. Bruch

STATISTICAL MECHANICS OF 2d SYSTEMS - MODELS AND CALCULATIONS

D. P. Landau

Department of Physics and Astronomy

University of Georgia

Athens, Georgia 30602

Relatively simple lattice gas (Ising) models are quite useful for describing the essential features of order-disorder transitions in adsorbed monolayers. Although mean-field theory offers a simple approach to determining phase diagrams, it is in many cases qualitatively as well as quantitatively incorrect. We shall describe a simple Monte Carlo computer simulation technique which is both accurate and flexible for the study of these models. Even with a limited number of near-neighbor competing interactions these models can show a rich variety of ordered states and phase diagrams. We shall use computer simulation results to demonstrate this richness and to point out potential pitfalls in the interpretation of the data. The triangular and square lattice gas models with competing near-neighbor couplings are shown to have simple phase transitions which fall into a wide range of universality classes: Ising, 3-state Potts model, 4-state Potts model, XY-model, XY-model with 6-th order anisotropy. In addition, tricritical and triple-points may appear, and incommensurate as well as degenerate ground-state phases may occur. Minor modifications of these models allow us to study multilayer adsorption, crystal growth, and surface-bulk competition in semi-infinite systems with modified surface coupling. More realistic models allow the continuous placement of particles and thus permits the study of 2-dimensional melting in systems without a substrate potential as well as commensurate-incommensurate transitions in continuous models with substrate potentials. Here molecular dynamics calculations can play an important role in providing another source of information about the behavior of these systems.

*Research supported in part by NSF grant #DMR-7926178 and AFOSR grant #80-0053.

Theory of Adatom-Adatom Interactions in Physisorption Systems

L. W. Bruch
Physics Department
University of Wisconsin-Madison
Madison, WI 53706

The present state of information about interactions among physically adsorbed atoms is reviewed. Such interactions have customarily been modelled with Lennard-Jones potentials, but there are now experiments which clearly show the inadequacies of such simple models. Examples are given to illustrate this. After a review of early characterizations of the adatom interactions, to provide a background for discussion of the detailed theories, methods of deriving information on the adatom interactions are described: empirical fits to experimental data, perturbation theories of intermolecular forces, and approximations to self-consistent field theories.

Information from virial coefficient data and from monolayer solid data is summarized. Estimates of the one-atom holding potential are described.

The application of perturbation theory to the evaluation of dispersion energy terms in the adatom interactions is outlined. Modelling of the substrate response with a dielectric continuum is discussed.

The evaluation of exchange-overlap energies for adsorbed closed-shell atoms is outlined. Different approximations, which are based on the density functional theory of the inhomogeneous electron gas, are described.

The relative magnitudes of terms in the adatom interactions are illustrated for the adsorption of inert gases on basal plane graphite and on Ag(111).

SESSION D

Tuesday, August 4

14:00 - 15:00

English-Math 101

M. van Hove, Chairman

Theory of Adatom-Adatom Interactions in Chemisorption Systems.
T. L. Einstein

Phase Transitions on W and Mo Surfaces.
P. J. Estrup, L. D. Roelofs and S. C. Ying

THEORY OF ADATOM-ADATOM INTERACTIONS IN CHEMISORPTION SYSTEMS

Theodore L. Einstein*

Department of Physics and Astronomy, University of Maryland
College Park, MD 20742

In chemisorption systems the interactions between adatoms are at least an order of magnitude smaller than the binding energy and also smaller than the binding energy difference of adsorption in various possible site symmetries on a surface. Thus, the lattice gas model provides a good description for these systems. Moreover, at the temperatures at which order-disorder transitions of the overlayers occur, coverage is fixed. Due to the small size of the interactions, the low symmetry of the problem, and the difficulty in calculating interaction energies (as opposed to one-electron band structures), progress in obtaining quantitative results from first principles calculations has not been so successful as in other fields of surface physics. (On the other hand, the weakness of the interaction makes self-consistency considerations less important than for single adatoms in semi-empirical calculations.) An alternative approach for theorists, which provides little insight into underlying mechanisms but produces better numbers, is to perform Monte Carlo simulations of overlayer phase diagrams obtained from LEED and other experimental techniques; the adatom-adatom interactions are the input parameters, which are adjusted to optimize fit. Both approaches will be surveyed.

The pairwise interaction between adatoms is generally attributed to indirect coupling via the substrate electronic structure, indirect elastic coupling, or dipole-dipole repulsions. Each will be described. The first-mentioned is of most importance in systems with neutral adsorption on metallic single-crystals. Its qualitative features and order of magnitude can be readily understood using simple tight-binding models. Detailed calculations have also been done using jellium substrates, which are of limited applicability to the transition metal substrates of most interest. Attempts at improved accuracy by using a d-band (5-fold degenerate) tight-binding model were not too successful. (The number that could be compared with a field ion microscopy result was too large by a factor of 5.) Very recent work using clusters embedded in jellium offers exciting hope of better agreement. Two other mechanisms proposed for specific systems will also be mentioned: a band stretching and bending model for O/W(110) and a large van der Waals interaction (due to expanded atomic p-orbitals) for O/Ni(100). Note that in calculations of pair interactions, accuracy to within a factor of two would be a significant feat. Direct interactions due to overlap between adatoms will be extremely important at small separations. Energy calculations are very hard but band structure effects have been computed.

Based on the dominant atom-pair interactions, one can readily deduce most qualitative features of the temperature-coverage phase diagram. With Monte Carlo simulations, quantitatively-accurate phase boundaries can be drawn. Simulations have been carried out for such systems as O/Ni(111), H/Ni(111), O/W(110), and H/W(100). The results will be given along with some comment on the degree of accuracy to be expected based on the limited number of interaction parameters typically treated. The role of three-atom interactions will be noted; these effects will be discussed in more detail in a contributed paper by Norman C. Bartelt. Finally, the existence of minor substrate reconstructions in systems previously thought ideal, particularly O/Ni(111), is explored as an impediment to quantitative understanding.

*Supported by Department of Energy under grant DE AS05-79ER-10427.

PHASE TRANSITIONS ON W AND Mo SURFACES.* P. J. Estrup, L. D. Roelofs and S. C. Ying, Department of Physics, Brown University, Providence, RI 02912.

In recent years there has been a very strong experimental and theoretical interest in the (001) surfaces of tungsten and molybdenum. These substrates display a multitude of surface phases as a function of temperature and adsorbate coverage. Many of the phases are known to involve not only a two-dimensional ordering of the adsorbed species but also a distortion of the substrate. We review results for clean W(001) and H/W(001) for which the experimental information is exceptionally detailed. Thus, evidence has been obtained by low-energy electron diffraction (LEED) concerning the long-range order of the phases, and by ion scattering, electron energy loss spectroscopy (ELS), electron stimulated desorption (ESD), and photoelectron spectroscopy (UPS) concerning the local structure. The results indicate that there are several qualitatively different phase transitions in these systems. We consider the nature of some of them, i.e., whether they are first-order or continuous, and what the appropriate order parameters and symmetries are. In so doing we will also deal with the question of whether these are properly defined phase transitions. Because of the intrinsic instability of the clean surface, the lattice gas model does not provide an adequate description. We present a generalized lattice gas model allowing for substrate atom displacements, and comment briefly on proposed mechanisms for the instability. The model has been applied to H/W(001) and a mean-field treatment is found to provide a satisfactory explanation of the main features of the phase diagram such as the enhancement of the $c(2 \times 2)$ phase and the switching of the substrate atom displacement by H. We also discuss a recent study of this model, going beyond mean field. In particular we will show that the $(1 \times 1) \rightarrow c(2 \times 2)$ transition has an order-disorder character. A cross-over to a displacive regime can occur at higher temperatures.

*Supported by the Brown University Materials Science Program and the National Science Foundation.

SESSION E

Wednesday, August 5

09:00 - 13:00

English-Math 101

T. L. Einstein, Chairman

Surface Diffusion.
D. A. King

Surface Reactions With Multiple Surface Phases
L. D. Schmidt

Phase Transitions on Nickel Single Crystal Surfaces at the Curie Temperature.
J. C. Hamilton and T. Jach

Synchrotron X-ray Study of Monolayer Xenon Melting
P. A. Heiney, R. J. Birgeneau, G. S. Brown, P. M. Horn,
D. E. Moncton and P. W. Stephens

Chemisorption on Stepped Surfaces and Adatom Binding Energies.
P. Kleban

SURFACE DIFFUSION

by

David A. King
Donnan Laboratories
University Liverpool
L69 3BX, UK

Recent advances in the study of diffusion of adsorbed species on single crystal surfaces¹, with a particular emphasis on the role of natural interactions between adsorbates and order-disorder phenomena will be reviewed. The diffusion coefficient D is defined as the proportionality constant between the diffusion current and the coverage gradient. Experimental results are usually expressed in terms of an activation energy barrier for diffusion, E_m , and the diffusivity, D_0 , defined by $D = D_0 \exp [-E_m/RT]$. In turn, assuming that diffusion occurs by intersite hopping by a mean-square jump distance a_2 with a frequency factor ν , the diffusivity is given by $D_0 = \nu a_2^2/4$ in two dimensional diffusion. With negligible activation energy for diffusion, D_0 is estimated as $3 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$, a useful guide in the consideration of experimental results.

The advantages and disadvantages of techniques used for measuring D_0 and E_m , are briefly surveyed. These include coverage gradient methods, in which a boundary between clean and adsorbate covered regions is formed, either on microscopic field emitter tips or macroscopic crystals, and a homogeneous coverage method developed by Gomer in which static fluctuations in coverage within a small area of a field-emitter tip are analysed.

Results obtained for the diffusion of (a) weakly bound states over sites filled by chemisorbed species, (b) molecular chemisorbed states, particularly CO, and (c) chemisorbed adatoms are reviewed. For physisorption states E_m is generally between 30 and 50 percent of the adsorption heat q ; for molecular chemisorption of CO, E_m is reportedly between 50 and 100 percent of q ; and for adatoms such as H, N and O, E_m is between 10 and 20 percent of the adatom-substrate bond energy. Diffusivities have been reported over the range $10^{-5} \leq D_0 \leq 0.3 \text{ cm}^2 \text{ s}^{-2}$, implying activation entropies for diffusion of between 0 and 45 J/mole/K. Particular emphasis is given to the system O on W(110), and an attempt is made to correlate the detailed diffusion results for this system, including recent work of Morris and King, with the character of island dissolution and order-disorder transitions studied by Lagally and co-workers. Crystal plane specificity of diffusion parameters and anisotropic effects on a given crystal plane are also discussed.

¹D. A. King, J. Vac. Sci. Technol. 17 (1980) 241.

SURFACE REACTIONS WITH MULTIPLE SURFACE PHASES

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We shall consider the possible role of multiple surface phases in multiple adsorbate and reacting systems. Phases have been shown to exist in some simple coadsorption systems, and it is probable that they occur in many catalytic reactions and may produce some interesting behavior. Such surface systems are open, have several components, and are not in thermodynamic equilibrium. Thus, we have a much more complicated situation than those discussed by others at this conference, and we shall in many cases be limited to qualitative considerations. However, these ideas suggest new directions for inquiry and may have technological importance.

Many (most) surface reactions cannot be explained by Langmuir Hinshelwood kinetics, the one-state noninteracting model of a reaction on a surface. Among the unusual types of observed behavior are: 1) steady state multiplicity, 2) hysteresis, and 3) rate oscillations. We shall show that each of these may be caused by multiple surface phases. For reactions of CO, NO, and HN_3 on Pt, there is fairly clear evidence of this correlation.

Much of the discussion will be centered around dilute-condensed phases with the assumption that systems are near adsorption-desorption equilibrium. For reacting systems this leads to easily visualized consequences.

For a unimolecular reaction $\text{A} \rightarrow \text{products}$ with only one species adsorbed there will be multiple phases if adsorbate-adsorbate interactions are attractive and temperatures are low. If the rate is proportional to surface density, there should be a discontinuity in rate as the reactant pressure is varied with the size of the discontinuity decreasing as the critical temperature of the surface phase is approached. Reaction may occur only in the dilute phase, only in the condensed phase, or only at the boundary, and these situations predict unusual rate behavior as functions of reactant pressure and temperature.

For a bimolecular reaction $\text{A} + \text{B} \rightarrow \text{products}$, the solubility of one species in islands of the other becomes important. With A-B attractions both molecules are always in intimate contact, while with sufficient A-B repulsions the reactant molecules can react with each other only at island boundaries.

Whenever there are multiple species or when reaction occurs at an island boundary, island size becomes an important parameter. This will depend on deposition conditions and on surface defects, and we may expect strong variations in rates with surface imperfections and with the extent of annealing of the adsorbate layer. The shapes of islands and their configuration is also important because the island edge length is not a unique function of adsorbate density even for fixed nucleation sites. Several configurations are possible, depending on whether the coverage is increasing or decreasing, and this should yield rate multiplicity and possibly rate oscillations.

Finally, the reaction may perturb the adsorbate configuration if it is sufficiently fast. As examples, reaction will tend to create holes in the adsorbate layer in a multiple adsorbate system, and for a sufficiently fast reaction surface diffusion becomes important as the adsorbed molecule has the choice of diffusing to an island or reacting.

PHASE TRANSITIONS ON NICKEL SINGLE CRYSTAL
SURFACES AT THE CURIE TEMPERATURE*

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ABSTRACT

Stepped surfaces vicinal to the (111) surface of nickel have previously been reported to undergo reversible changes in morphology in ultra-high vacuum at temperatures in the range 350°C-400°C.¹ By using low-energy electron diffraction (LEED) to monitor step height and periodicity, and simultaneously recording the AC permeability of nickel crystal samples, we have determined that the rearrangement transitions of both (111) x 5° [110] and (111) x 10° [110] surfaces begin at the Curie temperature. The rearrangements have approximately 25°C of width and occur reversibly with little observed hysteresis. They can be explained by a discontinuity in the surface free energy at the Curie point. We interpret this as the first evidence of a structural phase transition coupled to the ferromagnetic transition.

Reversible segregation of carbon to these surfaces and to the (111) surface of nickel has also been observed in the immediate vicinity of the bulk Curie temperature using Auger spectroscopy. All of these surfaces were free of carbon and other impurities at temperatures above the Curie point. Below the Curie point fractions of a monolayer of carbon were present. The carbon Auger peaks were carbide indicating that segregation (not precipitation) was occurring at the Curie point. From the data we infer a change of >0.2 eV/atom in the heat of segregation of carbon to the Ni(111) surface at the Curie temperature.

¹H. V. Thapliyal and J. M. Blakely, J. Vac. Sci. Technol. 15, 600 (1978).

* Research supported by the U.S. Department of Energy

Synchrotron X-ray Study of
Monolayer Xenon Melting

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Abstract

We have studied the melting of xenon adsorbed on ZYX exfoliated graphite as a function of pressure and temperature. At 112K we see clear evidence of liquid-solid coexistence. At 150K the liquid phase evolves continuously to a correlation length of at least 200 Å. The transition to the solid phase takes place over a temperature range of less than one degree.

CHEMISORPTION ON STEPPED SURFACES AND ADATOM BINDING ENERGIES*

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We report the results of a theory of chemisorption on stepped surfaces for systems which may be modeled by a lattice gas in thermodynamic equilibrium. We mention several results, including a general expression (in single-scattering approximation) for the LEED (Low Energy Electron Diffraction) intensity for an overlayer on a stepped substrate including the effects of disorder. In addition we argue that a comparison of LEED results for flat and stepped substrates can determine the sign of the change in adatom adsorption energy at terrace edge sites. This is illustrated by a Monte Carlo calculation of O on a certain stepped W(110) surface, where we find the binding energy to be less strong on either terrace edge site than on the flat surface. We also argue that in general the same information can be gleaned by a very simple comparison of appropriate LEED features. This conclusion is supported by a series of calculations on one-dimensional models.

*supported in part by the Office of Naval Research and a Stauffer Chemical Company grant of Research Corporation

POSTER SESSION F

Wednesday, August 5

15:00 - 17:00

English-Math Building Lobby

W. N. Unertl, Chairman

DISCUSSION

17:00 - 18:00

English-Math 101

Discussion Leaders: P. Estrup
L. D. Schmidt
R. L. Park

- F-1 Films and Layers
- F-2 Phase Behavior Involving Substrate Atoms
- F-3 Kinetic Phenomena
- F-4 Related Topics

POSTER SESSION

F-1

FILMS AND LAYERS

Wednesday, August 5

15:00 - 17:00

English-Math Building Lobby

Observation of Step-Wise Solid Layer Nucleation of ^4He on Grafoil
J. D. Maynard, G. J. Jelatis and J. A. Roth

Phase Separation in ^3He - ^4He Mixture Films
F. M. Ellis and R. B. Hallock

Superfluid Onset in Thin Helium Films
G. B. Hess, R. J. Muirhead and J. G. Dash

Onset of Superflow in ^4He Films on Mylar
J. Maps and R. B. Hallock

Dislocation Pair Disruption in Layered Superconductors
C. Deutsch and S. Doniach

Forces Resulting From Order Imposed at a Liquid-Solid Interface
R. G. Horn, J. N. Israelachvili and H. K. Christenson

Phase Transitions of Surface Electrons
A. Isihara and L. Ioriatti, Jr.

Surface Segregation on PtCu Alloys: Evidence for Crystal Face Dependence
I. Lindau, M. L. Shek and W. E. Spicer

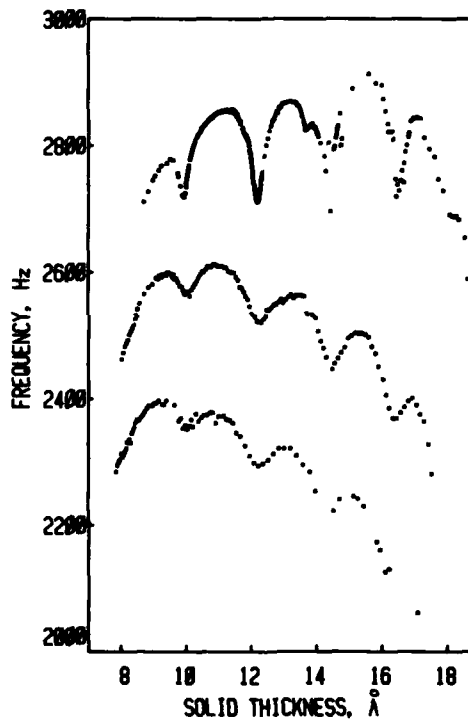
OBSERVATION OF STEP-WISE SOLID LAYER NUCLEATION OF ^4He ON GRAFOIL

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The Pennsylvania State University
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Currently there is some interest in the role of surfaces in the nucleation of solid from the liquid phase.^{1,2} We have recently investigated the growth of solid ^4He on Grafoil and have observed step-wise solid layer nucleation which is quite sharp at low temperatures (below 1.4K). The estimated incremental layer thickness of $2.3 \pm 0.2 \text{ \AA}$ is somewhat less than the one-half c-axis length for the ^4He hcp structure. We are not aware of a theory which predicts this behavior. It is hoped that our data will stimulate some interest in the role of the surface on the multi-layer liquid-solid transition.

The solid layer nucleation was probed with measurements of the He II fourth sound velocity which depends on the Grafoil pore size and subsequently reflects the thickness of the solid formed on the pore walls. Fourth sound resonance frequencies were measured as a function of pressure (from SVP to the solidification curve) along eight isotherms (from 1.0K to 1.7K). From above 10 bar to within about 1 bar of the solidification curve, periodic structure, quite sharp at the lower temperatures, was observed in the fourth sound pressure dependence. In order to interpret this behavior in terms of solid layer nucleation, the measured pressure P was related to a total solid thickness d with a Franchetti calculation: $d = [\bar{\lambda} - \bar{\lambda}^{1/3}] (P_s - P)^{-1/3}$ where P_s is the solidification pressure for the isotherm. Plots of the fourth sound resonance frequency versus d are shown in the figure. The periodic structure (with period $2.3 \pm 0.2 \text{ \AA}$) is clearly evident and we interpret this as evidence of step-wise solid layer nucleation. To date, Grafoil is the only fourth sound medium to display such behavior.



Fourth sound resonance frequency versus total solid thickness. 1.0K (upper), 1.4K (center), and 1.5K (lower).

1. Eckstein, Y., Landau, J., Lipson, S. G., and Olami, Z., Phys. Rev. Lett. 45, 1805 (1980); Balibar, S., Castaing, B., and Laroche, C., J. Physique Lett. 41, L-283 (1980)
2. Landau, J., Saam, W. F., Phys. Rev. Lett. 38, 23 (1977)

Phase Separation in ^3He - ^4He Mixture Films*

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Abstract

Third sound measurements in an experimental cell designed to unambiguously characterize many of the properties of mixture films have been made at temperatures in the range 0.3-1.5K and for film concentrations, x , $0 \leq x \leq 0.5$. These measurements can be understood within the context of a straightforward theory of layered superfluid hydrodynamics and demonstrate phase separation.¹ The phase separation is layered due apparently to the strong van der Waals potential. This layered phase separation appears to be the natural state for mixture films of thickness, d , greater than six atomic layers such as we have studied to date. Our studies suggest that lateral phase separation of the type studied theoretically by Berker and Nelson² may be visible only in much thinner films - films with a mobile thickness less than one atomic layer.

*Supported by the National Science Foundation.

¹F.M. Ellis, R.B. Hallock, M.D. Miller and R.A. Guyer, Phys. Rev. Letters **46**, 1461 (1981).

²A.N. Berker and D.R. Nelson, Phys. Rev. **B19**, 2488 (1979).

Superfluid Onset in Thin Helium Films.*

G.B. HESS,[†] R.J. MUIRHEAD, and J.G. DASH, University of Washington, Seattle, WA.

We have studied the onset of superfluidity in thin helium films on several substrates, using the technique of thermally driven superfluid flow. Measurements on both sides of the Kosterlitz-Thouless transition can be compared with theoretical predictions, which have been worked out in some detail by Ambegaokar *et al.*¹ and Teitel.² The measured thermal resistance is proportional to the density of free vortices n_f , which should increase exponentially with the square root of the distance from the transition on the normal side. Evidence for this is presented for a gold-plated copper substrate. On a substrate of high thermal conductivity, the film resistance is shunted through the Kapitza boundary resistance. This situation is analyzed and shown to have favorable aspects for studying the onset region.

On the superfluid side of the transition there should be no free vortices at velocity $v = 0$, and at finite velocity, $n_f = Av^\alpha$, with exponent α proportional to the superfluid areal density. This power-law dependence arises from the logarithmic vortex-vortex interaction and is strikingly different from the three-dimensional case. On gold-plated copper we observe power-law behavior over about two decades in n_f , with reasonable values of α as a function of film thickness. Measurements on highly ordered pyrolytic graphite (HOPG) give a similar power law, although for technical reasons only a limited range is accessible.

It has long been recognized that superfluid onsets on different substrates occur roughly on a universal curve in the variables T and vapor pressure p (not thickness). We confirm that the onset on HOPG, which is believed to be clean and uniform, is almost exactly coincident in these variables with the onset on pyrex, gold-plated copper, and epitaxial gold (111) on mica.

* Research supported by the National Science Foundation.

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1. V. Ambegaokar, B.I. Halperin, D.R. Nelson, and E.D. Siggia, Phys. Rev. B **21**, 1806 (1980).

2. S. Teitel, preprint.

Onset of Superflow in ^4He Films on Mylar*

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Abstract

The superfluid transition in thin ^4He films is investigated by studying the thermal conductance of the ^4He film as a function of film thickness in the temperature range $1.25 < T < 2.1\text{K}$. One end of a single mylar strip is wound with a wire heater. Attached directly to the surface of the mylar are carbon resistors which serve as thermometers. The temperature difference is monitored for constant power applied to the heater as the film is gradually thickened. The onset of superflow is marked by a dramatic drop in the observed temperature difference. The critical thickness, d_c , needed for superflow is obtained as a function of temperature. It is found¹ to fit the form $T_c(d) = T_\lambda(1 - A/d^\gamma)$ where $\gamma = 1.4 \pm 0.1$ and $A = 1.6 \pm 1$. The theoretical work of Ambegaokar, Halperin, Nelson, and Siggia² (AHNS) predicts $\gamma = 3/2$. In addition, comparison is made to the prediction of AHNS for the thermal conductance of the film in the neighborhood of onset. The abrupt rise in the superfluid areal density ρ_s at onset is calculated from the fit of the full onset curve and the relation $\rho_s = \rho_s^{(b)} d\Phi(x)$, where $\rho_s^{(b)}$ is the bulk superfluid density and $\Phi(x)$ is a function which describes the crossover from two to three dimensions. The value of $\rho_s(T_c^-)/T_c$ is found to be $\sim 4.5 \times 10^{-9} \text{ g/cm}^2\text{K}$ independent of T_c .

*Supported by the National Science Foundation

¹J. Maps and R.B. Hallock (to be published)

²V. Ambegaokar, B.I. Halperin, D.R. Nelson and E. Siggia, Phys. Rev. B21, 1806 (1980).

DISLOCATION PAIR DISRUPTION IN LAYERED SUPERCONDUCTORS

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We consider the melting transition in a stacked system of very weakly coupled Abrikosov lattices in superconducting films separated by insulating spacers¹.

- At finite temperature, disorder is induced in the lattice structure by the formation of dislocation pairs, very weakly coupled between sheets for pair separations smaller than a critical distance² $r_c \sim g^{-1/2}$. g is a vanishingly small interplanes coupling constant².

- As the temperature is increased towards the 2d vortex lattice melting temperature the dislocation pair separation is inhibited for spacings $> r_c$ by the formation of discommensuration lines joining the dislocations². The melting of the vortex lattice thus takes place via a first-order transition induced by transverse phonons.

- Toward this end, we do consider a modified Kosterlitz-Thouless scheme with a quarklike interaction² (ξ_0 = coherence length)

$$q^2 \ln \left| \frac{r}{\xi_0} \right| e^{-r/\xi_0} + \sqrt{g} \left| \frac{r}{\xi_0} \right|, \quad (1)$$

taking into account at $r \geq r_c$, transverse coupling with nearby planes. Eq. (1) prevents pair breaking and genuine inplane phase transition.

Nonetheless a pair disruption is still possible by matching a transverse phonons free energy with the difference ($r > r_c$) =

Free energy of a logarithmic pair³

- Free energy of a quarklike pair.

As a result we get a very smooth crossover

$$T_{3D} \approx T_{2D} + \frac{\text{const.}}{(\log \log \frac{1}{g})^2}, \quad g \rightarrow 0$$

at the melting transition.

¹S.T. RUGGIERO, T.W. BARBEE, Jr., and M.R. BEASLEY, Phys. Rev. Lett. 45, 1299 (1980).

²S. DONIACH, in Ordering in two dimensions, Ed. S.K. SINHA, North-Holland,

FORCES RESULTING FROM ORDER IMPOSED AT A LIQUID-SOLID INTERFACE

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The presence of a solid surface may impose some ordering on the molecules of a liquid adjacent to it; in particular it may cause the molecules to form *layers* parallel to the surface. When two surfaces approach each other the layering due to one will reinforce that due to the other at surface separations which allow an integral number of layers; at intermediate distances it will interfere with it. The energy of the system therefore passes through alternate maxima and minima as the separation is changed, which gives rise to a *structural force* between the surfaces.

We have measured such effects in various liquids: octamethylcyclotetrasiloxane, cyclohexane, carbon tetrachloride and the nematic liquid crystal 4'-n-pentyl 4-cyanobiphenyl. In the case of the nematic liquid crystal the order imposed by the surfaces causes a *smectic* (layered) phase to exist in films less than 15 nm thick. For each of these liquids the force law is not the monotonic dispersion attraction that would be expected if the liquid was assumed to be a continuous medium, but is an oscillatory function of the separation between the solids, with the periodicity of the oscillations corresponding to the size of the liquid molecules. Typically between five and ten oscillations are measurable as the surface separation increases from zero to several nm.

The force was measured between two mica sheets which are molecularly smooth, using the apparatus developed by Israelachvili and Adams (J. Chem. Soc. Faraday Trans. I 74 (1978) 975). In this the force is determined to $\pm 10^{-7}$ N using a spring whose deflection is measured very accurately, and the separation between the mica surfaces is determined to ± 0.1 nm using an optical interference technique. The optical technique can easily be used in much simpler experiments to measure both the thickness and the refractive index of adsorbed films on the mica.

Phase Transitions of Surface Electrons.* A. Isihara and L. Ioriatti, Jr., Statistical Physics Laboratory, Department of Physics and Astronomy, State University of New York at Buffalo, Buffalo, N. Y., 14260.-- The two-dimensional electron systems such as those formed at semiconductor interfaces show prominent many body correlation effects in wide density ranges. We have developed a new very powerful method of treating the correlations of these electrons. According to this theory, the energy changes its analytical character at $r_s = 1.414$, around which the Hartree-Fock approximation is not valid and the system must be considered to be in a liquid-like state. It has been revealed recently that the two valleys for the electrons in the (001) direction of the silicon MOSFETs may not be equally populated. We shall show such a valley population phase transition can indeed take place due to the strong correlations. Furthermore, in the presence of a magnetic field, the spin-up and -down states of the electrons are not occupied equally by the electrons. This population difference, coupled with the strong electron correlations, is expected to cause a phase transition from a paramagnetic state into a ferromagnetic state.

*Work supported by the ONR.

SURFACE SEGREGATION ON PtCu ALLOYS: EVIDENCE FOR CRYSTAL FACE DEPENDENCE

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In this paper, we report on experimental evidence that the surface segregation of Cu in a PtCu alloy depends on the crystallographic orientation. Both Auger electron spectroscopy and photoemission show that the Cu surface segregation is at least twice as large on the (110) face as on the (111) face. For an alloy with the bulk composition $\text{Pt}_{0.98}\text{Cu}_{0.02}$, we found that the top 3 to 4 Å of the surface region contains about 10% Cu for the (110) surface and about 4.5% for the (111) surface. If it is assumed that the Cu segregates to only the topmost layer, the corresponding concentrations will be 28% and 8%, respectively. With the exception of two recent reports [1,2] for the CuNi system, we believe that this is one of the first alloys for which the crystal face dependence of the surface segregation has been unambiguously established.

The observed Cu segregation is in qualitative agreement with the broken-bond model [3], which predicts that the surface segregation should decrease as $(110) > (100) > (111)$. However, the broken-bond model is not sufficient to provide a quantitative comparison between theory and experiment. The limitations of the model will be discussed, particularly in view of the fact that the electronic interactions in the alloy may considerably modify the broken-bond energies of the constituent atoms (as compared to the atoms in the pure solids). It is noteworthy that the photoemission data show the Cu-derived valence electronic structure of PtCu to be significantly different from the pure Cu.

References

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2. C. R. Brundie and K. Wandelt, J. Vac. Sci. Technol. 18, No. 1 (1981).
3. F. L. Williams and D. Nason, Surf. Sci. 45, 377 (1974).

POSTER SESSION

F-2

PHASE BEHAVIOR INVOLVING SUBSTRATE ATOMS

Wednesday, August 5

15:00 - 17:00

English-Math Building Lobby

Phase Transitions for CO and NO Adsorption on Pt(110) Surfaces
T. E. Jackman, J. A. Davies, P. R. Norton, D. P. Jackson and W. N. Unertl

Surface Phase Transitions During CO Adsorption and Desorption on Pt(110)
P. Hofmann, S. R. Bare and D. A. King

Surface Barrier Resonances in Reels
J. Didham and R. F. Willis

Adsorbate-Induced Restructuring of Mo and W Surfaces
S. Semancik and P. J. Estrup

Chemisorption-Induced Phase Transitions and Adatom Interactions on GaAs(110)
P. Skeath, C. Y. Su, P. W. Chye, I. Lindau and W. E. Spicer

Phase Diagram of Oxygen on Nickel(100)
D. E. Taylor and R. L. Park

Incommensurability of the Clean Mo(100) Surface
A. Fasolino and E. Tosatti

The Surface Reconstruction and Relaxation of the (001) Surface of Mo and W
N. Hamada, I. Terakura and K. Terakura

Phase Transitions of MO-5%Re(100) and Stepped W(100) Surfaces
G.-C. Wang, D. M. Zehner and H. Eaton

Determination of Surface Magnetic Structures Near the Phase Transition
Critical Temperature by Polarized Low Energy Electron Diffraction: Ni
(110) System
S.-W. Wang

Phase Transitions for CO and NO
Adsorption on Pt(110) Surfaces

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Chalk River Nuclear Laboratory
Chalk River, Canada

and

W. N. Unertl*†, University of Maine, Orono, Maine

We have used Rutherford ion backscattering, nuclear microanalysis, low-energy electron diffraction (LEED) and thermal desorption to study the surface phases formed during the adsorption of NO and CO on Pt(110) surfaces.

The complete temperature vs. CO coverage (T vs. θ) phase diagram has been determined for CO coverages up to one monolayer and substrate temperatures above 160 K. Adsorption isobars were used to determine ΔH , the isosteric heat of CO adsorption, during the (1x2) to (1x1) phase transformation. ΔH is 160 ± 15 kJ/mole for coverages up to about one-half monolayer and decreases at higher coverages. The clean surface (1x2) structure completely transforms to a (1x1) structure for $\theta \approx 0.75$ and thermal desorption spectra indicate the presence of at least two adsorption states. For CO coverages above 0.75 monolayer, a (2x1) structure with p1g1 symmetry forms. The phase boundary between the (1x1) and (2x1) p1g1 structures at $\theta \approx 0.75$ is sharp. Its variation with CO pressure and substrate temperature yields an isosteric heat of 135 ± 5 kJ/mole. CO adsorption saturates at $\theta \approx 1$ ($0.9 \pm 0.05 \times 10^{15}$ CO/cm²). Rutherford backscattering measurements show that platinum atoms are not significantly displaced from bulklike positions in any of the (1x2), (1x1) or (2x1) p1g1 phases. This observation, when combined with the strong half-order LEED intensities, rules out the paired row model of the (1x2) surface in which adjacent [110] rows of surface atoms are displaced toward each other. It is completely consistent with every other [110] row of atoms missing.

If the crystal is cooled below 250 K before CO is adsorbed, a new metastable phase with c(8x4) LEED pattern forms. Rutherford backscattering shows that an entire monolayer of platinum atoms is displaced.

Similar behavior is observed for NO adsorption on Pt(110).

*Supported by NSF grants DMR77-28543 and DMR-8020840.

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Surface phase transitions during CO adsorption and desorption on Pt{110}

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While undertaking a multitechnique study of the chemisorption of CO on Pt{110}, we investigated in detail the various surface phase transitions occurring in this system with continuous monitoring of LEED beam intensities, the CO $1\pi/5\sigma$ level intensity observed in ARUPS and thermal desorption spectra (TDS).

The chemisorption of CO is known to lift the reconstruction of the clean, reconstructed Pt{110} - (1 x 2) surface and to form an ordered phase at high coverages belonging to the space group $p1g1$. Our results clearly indicate that another phase exists at very low coverages ($\theta \leq 0.2$), where isolated species are co-existent with small islands of CO on Pt{110} - (1 x 1). The isolated singleton species adsorb upright on the Pt-(1 x 2) surface while at higher coverages on the (1 x 1) surface the CO axis is considerably tilted away from the surface normal. Island growth, characteristic of attractive interactions between CO molecules, proceeds until a coverage of ~ 0.5 , when the half order spots in LEED are no longer visible. A single peak is observed in TDS. At $\theta > 0.5$ a shoulder at lower temperatures develops in the desorption spectra due to repulsive CO-CO interactions; the LEED pattern remains (1 x 1).

The well ordered (2 x 1) $p1g1$ phase can be formed at saturation coverage by annealing the surface in an ambient pressure of CO. Without annealing, defect sites due to imperfect lifting of the (1 x 2) surface reconstruction are thought to inhibit the formation of the ordered phase. The latter conclusion stems from various TDS-experiments involving different heating rates, imperfect (Ar^+ -bombarded) surfaces as well as experiments with preadsorbed NO. LEED I(V) spectra reveal that no major lateral displacements of Pt-atoms are involved during the formation of the ordered $p1g1$ phase. The (2 x 1) $p1g1 \rightarrow (1 \times 1)$ order-disorder transition is reversible.

SURFACE BARRIER RESONANCES IN REELS

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Abstract for International Conference on Phase Transitions on Surfaces at
University of Maine, Orono 3-7 August 1981

High resolution reflection electron-energy-loss studies of two-dimensional energy band structure of surface barrier resonances on W(100) suggest that they are sensitive to surface reconstruction. The energies of these resonances appear to fit a simple Rydberg type series of levels for a smooth monotonic surface barrier potential, the "ionization levels" of which are determined by the grazing emergence conditions for diffraction beams. The behaviour of the intense ground state level suggests that the lower order resonances are sensitive to the two-dimensional Fourier components of the potential variation in the surface. The crossing of the resonances propagating along specific symmetry directions produces "hybridization gaps", from which it is possible to estimate these two-dimensional Fourier co-efficients. Strong intensity in the elastically-scattered (00) electron beams is only found for energies corresponding to energy gaps in the surface projection of bulk electronic states. At impact energies corresponding to these energy gaps, the surface electronic potential is sensitive to the atomic ordering in the surface interaction region. We report preliminary results for the temperature dependence of the W(100) $C(2 \times 2) \rightarrow P(1 \times 1)$ surface reconstruction under these conditions.

ADSORBATE-INDUCED RESTRUCTURING OF Mo AND W SURFACES

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and
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Previous investigations of Mo(001) and W(001) have shown that displacements of the outermost atoms can be induced by cooling these crystals, or by adsorbing hydrogen on them. It has been found that other adatoms (e.g., C, N, and O) give rise to LEED patterns, intensity vs voltage curves, work function changes and electron stimulated desorption yields that are very similar to those observed for hydrogen adsorption on these substrates. These data are difficult to explain in terms of an overlayer bound to a rigid lattice, and it is concluded to be likely that all of these adsorbates cause displacements of the surface metal atoms. In order to account for electron scattering from the adlayer, it is also proposed that the site occupation probability for adatoms is coupled to the substrate distortions. Variations in the activation energies for desorption and dissociation processes are apparently consequences of the coverage-dependence of the adsorbate-induced restructuring.

*NRC-NBS Postdoctoral Research Associate

Chemisorption-Induced Phase Transitions and
Adatom Interactions on GaAs(110)*

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A wide range of behavior in chemisorption-induced phase transitions, depending on the adatom system, has been observed on GaAs(110). In some systems a strong chemical interaction between adatoms is also seen. Results from three adsorbate systems (oxygen, Sb, and the column 3 metals) are compared. Oxygen chemisorbed on GaAs(110) completely disorders the surface, even at low ($\theta \leq \frac{1}{2}$ monolayer) coverage. Deposition of one monolayer Sb yields a very well ordered overlayer with no change in unit cell dimensions (1×1). Neither a change in GaAs surface lattice reconstruction nor long range order in the overlayer is observed after deposition of column 3 metals (Al, Ga) on the (110) surface. Strong evidence exists for two dimensional (one atom thick) raft formation with submonolayer coverages of Al or Ga. Temperature dependent studies ($80^\circ\text{K} \leq T \leq 400^\circ\text{K}$) suggest that 'annealing' of Ga overlayers occurs at $\sim 270^\circ\text{K}$. The column 3 adatom results are briefly discussed in terms of competition between adatom-adatom and adatom-substrate bonds. These results support the view that the reconstruction of GaAs(110) is determined by local valence bonding considerations. Most importantly, it is concluded that chemical interactions between adatoms are of primary importance in the more 'metallic' adatom systems.

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PHASE DIAGRAM OF OXYGEN ON NICKEL(100)

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We have used LEED and AES to study the phases of chemisorbed oxygen on Ni(100) in the coverage range of 0.1 to 0.5 monolayer and the temperature range of 100°K to 900°K. The p(2x2) structure of oxygen on Ni(100) is observed to undergo a reversible order-disorder phase transition with hysteresis ($T_c = 605^\circ\text{K}$ at $\theta = 0.25$ monolayer), but it is possible this hysteresis is not intrinsic to the transition. The oxygen overlayer begins dissolving into the bulk nickel at about the same temperature as that where the p(2x2) structure disorders, which necessitates heating and cooling the sample through the critical region very swiftly in order to see the transition without losing oxygen from the surface. The observed hysteresis may thus be a non-equilibrium effect, rather than an indication of a first order phase transition. The fact that bulk dissolution begins near the disordering temperature of the p(2x2) structure is not thought to be accidental, and is taken to mean that the highly mobile oxygen atoms of the disordered phase have a substantially increased probability of bulk dissolution as compared with those in an ordered phase. The p(2x2) structure is observed to initially form a short-range order, "island" phase at room temperature, as evidenced by broad half-order LEED beams. This island phase is seen to give way to the long-range order of the full p(2x2) structure upon annealing. The c(2x2) structure of oxygen on Ni(100) is seen to be very stable up to remarkably high temperatures, over 800°K, at which point the overlayer dissolves very rapidly into the bulk. An order-disorder transition similar to that of the p(2x2) structure is not seen.

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INCOMMENSURABILITY OF THE CLEAN Mo(100) SURFACE

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We show that the onset of incommensurability on Mo(100) can be explained -- in the framework of our soft surface phonon model of displacive transition metal surface reconstructions¹⁾ -- by an elastic energy gain connected with the mixing, away from the high-symmetry M point ($1/2, 1/2$), of a z-vibration component into the twofold degenerate (x,y) soft mode. We point out the clear analogy with other incommensurate systems^{2,3)}, but also one important difference, introduced by symmetry. Since the mode dispersion away from M is quadratic, no "Lifshitz terms" are present in the Landau expansion²⁾, which then takes an unusual form. A preliminary discussion of the effects of incommensurability in this case will be presented.

- 1) A.Fasolino, G.Santoro and E.Tosatti Phys. Rev. Letters 44, 1684 (1980); E.Tosatti in Modern Trends in the Theory of Condensed Matter, ed. by A.Pekalski and J.Przystawa, Springer (1980) p.501
- 2) V.Dvořák, in Modern Trends in the Theory of Condensed Matter, as above, p.447
- 3) V.Heine, J.D.C. Mc Connell, to be published

THE SURFACE RECONSTRUCTION AND RELAXATION OF THE (001) SURFACE OF MO AND W

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The reconstruction and the relaxation of the (001) surface of Mo and W are studied by using the tight-binding d band and the Born-Mayer repulsive potential. The d band parameters are set to reproduce band energies of ab initio band calculations at high symmetry points in the Brillouin zone and the parameters in the Born-Mayer potential are chosen to obtain the correct equilibrium lattice constant and the bulk modulus of the bulk crystal. First, we focus our attention to the mechanism of the relaxation and give an interpretation to the general trend that the contraction of the surface interlayer spacing is larger for a more loosely packed surface. Our study on the surface relaxation reveals that the (001) surfaces of Mo and W are unstable with regard to the $c(2 \times 2)$ mode with the atomic displacement within the surface plane. By calculating the energy change up to the fourth order of the atomic displacement, we determine the direction and the magnitude of the atomic displacement. Thereby we give a theoretical support to the Debe and King model with the atomic displacement of about 0.25Å, which is in fair agreement with the LEED analysis. We show that the presence of the surface state peak in the surface density of states near the Fermi level is substantial in the surface reconstruction, but that the Fermi line nesting is not a crucial ingredient. This is supported by the calculation of the response functions with and without electron-phonon interaction. However, this does not mean that the (001) surfaces of Mo and W are unstable for an arbitrary atomic displacement, unlike the conjecture by Inglesfield. In fact, the present calculation leads to the results that the surfaces are stable with regard to the (2×1) mode, for example.

PHASE TRANSITIONS OF Mo-5%Re(100) AND STEPPED W(100) SURFACES*

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Surface reconstructions observed on clean Mo(100) and W(100) surfaces by cooling the crystals below room temperature make possible the study of clean surface phase transitions,² the determination of the mechanisms responsible for reconstruction³ and the evaluation of two-dimensional statistical mechanical models which describe the phase transitions.⁴

We have used LEED, AES and XPS to investigate the effects of intrinsic and extrinsic impurities, and controlled surface defects on the clean surface phase transitions. A dilute binary alloy Mo-5%Re(100) surface and a stepped W(100) surface, with step edges parallel to the $\langle 11 \rangle$ direction and an average terrace width of 30 Å, were prepared and cleaned using standard procedures. AES and XPS results indicate a slight enrichment of Re in the surface region of the Mo-5%Re(100), consistent with predictions of a graphical approach for surface segregation. In contrast to the pure Mo(100) surface, where a quartet of extra LEED reflections are observed centered at the $(1/2, 1/2)$ positions, no nonintegral order reflections were observed for the clean alloy surface at crystal temperature as low as 160 K. However, when CO was adsorbed on the surface at low temperature, a quartet of extra reflections rotated 90° with respect to the reconstructed clean Mo(100) case was observed. The intensities and positions of these extra reflections were found to be coverage dependent.

For the clean, stepped W(100) surface, intense $(1/2, 1/2)$ reflections from two rotationally equivalent domains were observed below room temperature. This is contrary to a previous conclusion that a 20 Å inhibition distance could be associated with a step. The absence of splitting in the $(1/2, 1/2)$ reflections, however, is consistent with the conclusion of a theoretical study of reconstructed domains from a stepped W(100) surface using a lattice gas model.⁵

The interpretation of these observations will be discussed in terms of various driving mechanisms proposed for phase transitions.

1. Present address: Louisiana State University, Baton Rouge, LA 70803
2. T. E. Felter, R. A. Barker and P. J. Estrup, *Phys. Rev. Lett.* **38**, 1138 (1977); M. K. Debe and D. A. King, *Phys. Rev. Lett.* **39**, 708 (1977); *Surf. Sci.* **81**, 193 (1979).
3. E. Tosatti, *Solid State Commun.* **25**, 637 (1978); J. E. Inglesfield, *J. Phys. C* **12**, 149 (1979); K. Krakauer, M. Posternak and A. J. Freeman, *Phys. Rev. Lett.* **43**, 1885 (1979); I. Terakura, K. Terakura and N. Hamada, *Surf. Sci.* **103**, 103 (1981).
4. P. J. Estrup and R. A. Barker, in "Ordering in two dimensions", ed. by S. K. Sinha, Elsevier North-Holland (1980).
5. T.-M. Lu and G.-C. Wang, accepted by *Surf. Sci.* (1981).

*Research sponsored by the Division of Materials Science, U.S. Department of Energy, under contract W-7405-eng-26 with Union Carbide Corporation.

Determination of Surface Magnetic Structures Near the Phase
Transition Critical Temperature by Polarized Low Energy Electron
Diffraction: Ni (110) System*

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ABSTRACT

Temperature dependent polarizations of spin polarized low energy electron beams scattered by ferromagnetic Ni (110) surfaces were calculated in this work near the bulk phase transition Curie temperature. We used at $T = 0$ for each surface atom scattering potentials obtained from one-, three-, five-layer spin polarized thin film calculations¹ and spin polarized bulk Ni potentials.² For $T > 0$, these potentials were reconstructed by taking into account the temperature dependent magnetizations of surface layers.³ These layer dependent surface magnetizations were derived partly in our previous work⁴ using the simple mean field theory. From the reconstructed T-dependent and layer-dependent scattering potentials we calculated the diffracted electron intensities for spin-up and -down incident electron beams. Our results showed excellent agreement with experimental data and determined the magnetic structures of Ni (110) surface.

* Work supported by the Department of Energy under contract DE-AC03-76SF00515.

1. H. Krakauer, private communications.
2. V. L. Moruzzi, J. F. Janak and A. R. Williams, Calculated Electronic Properties of Metals, Pergamon, 1978.
3. S. W. Wang, Solid State Communications, 36, 847, 1980.
4. Bulletin of the American Physical Society, 26, No. 3, 356, March 1981.

POSTER SESSION

F-3

KINETIC PHENOMENA

Wednesday, August 5

15:00 - 17:00

English-Math Building Lobby

Non-Equilibrium Adatom Distributions From Irreversible Immobile Chemisorption
D. R. Burgess, J. W. Evans and D. K. Hoffman

Oscillatory Surface Mobility on ZnO
D. Kohl and G. Heiland

Kinetic Equations for Physisorption
H. J. Kreuzer

Two-Dimensional Diffusion Via the Vacancy Mechanism - an Exact Solution
B. Gralla and L. Gunther

A Study of the Flash Desorption of CO on a Ni(111) Single Crystal With
Small Angle Boundaries (SAB)
G. A. Sargent, J. L.-R. Chao and G. B. Freeman

NON-EQUILIBRIUM ADATOM DISTRIBUTIONS
FROM IRREVERSIBLE IMMOBILE CHEMISORPTION

By D. R. Burgess, J. W. Evans and D. K. Hoffman
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A chemisorption process is considered at temperatures where the mobility of the adatoms is negligible¹ and desorption can be ignored. Further it is assumed that the rate of adsorption onto suitably vacant sites is influenced by the configuration of the local environment. The cooperative effects could be determined by e.g., direct adatom-adatom interaction or by adatom perturbation of the phonon spectrum. Thus the adsorption process is irreversible and the distribution of adatoms is kinetically rather than thermodynamically determined.

A closed infinite hierarchy of rate equations may be developed for the probabilities of "effectively" connected subconfigurations of empty sites²⁻⁶. Larger hierarchies are required for more general configurations, e.g., "effectively" disconnected, and these couple back into the above minimal hierarchy⁷. Certain exact results are available for these equations. The one dimensional model can be solved exactly for an arbitrary range blocking interaction and range 1 cooperative tail. A shielding property of empty sites allows the truncation of the hierarchy^{4,7}. This allows the examination of such features as ordered filling, asymptotic decay of spatial correlations and island formation (clustering of a rather different nature than associated with equilibrium phase transitions). For more general interactions the hierarchy truncation involves some approximation. For the two dimensional model, it is possible to obtain an exact shielding property of empty sites (which, however, does not allow truncation of the hierarchy) and various cluster expansions in the density³ (which have some formal similarities to equilibrium expansions). Successively accurate truncation schemes have been developed for non-cooperative dimer adsorption². However for cooperative problems the solution is very sensitive to the choice of truncation scheme necessitating the simultaneous solution of many coupled equations.

¹ G. Ehrlich and F. G. Hudda, J. Chem. Phys. **35**, 1421 (1961).

² K. J. Vette, T. W. Orent, D. K. Hoffman and R. S. Hansen, J. Chem. Phys. **60**, 4854 (1974).

³ D. K. Hoffman, J. Chem. Phys. **65**, 95 (1976).

⁴ N. O. Wolf, D. R. Burgess and D. K. Hoffman, Surface Sci. **100**, 453 (1980).

⁵ N. O. Wolf, Ph.D. Thesis, Iowa State University, 1979.

⁶ I. R. Epstein, Biopolymers **18**, 765 (1979) and references therein.

⁷ N. A. Plate, A. D. Litmanovich, O. V. Noah, A. L. Toom and N. O. Vasilyev, J. Polymer Sci. (Chem. Ed.) **12**, 2165 (1974).

*Operated for the U.S. Department of Energy by Iowa State University under contract No. W-7405-Eng-82.

OSCILLATORY SURFACE MOBILITY ON ZNO

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The surface conductivity of ZnO crystals can be raised by annealing, exposure to atomic hydrogen or by photolysis. All these methods yield an oscillatory behaviour of surface conductivity and surface Hall mobility measured in ultrahigh vacuum as a function of the surface electron density. An example is given in the figure:

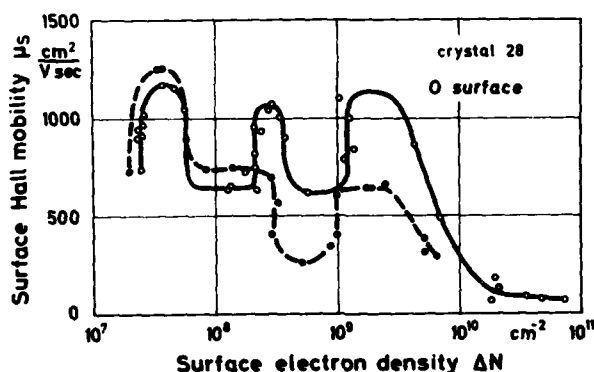


Fig. 1. Surface Hall mobility μ_s as a function of surface electron density ΔN generated by photolysis at 300 K (UV-irradiation). The open circles belong to measurements on the freshly cleaved surface. After the first run an oxygen treatment was used to remove the surface conductivity completely. The filled circles correspond to a second photolysis procedure.

A classical model of the accumulation layer on a compensated bulk shows that the width of a single maximum corresponds to a band bending variation of only one kT . Therefore the slopes of the maxima cannot be explained by bulk centers and surface states changing their condition of charge as a function of surface potential. In the photolysis treatment following oxygen exposure only the decreasing but not the increasing tail of the central maximum remains unchanged. The adjacent part of the curve seems to be displaced in parallel. Therefore the effect causing the central maximum is changed by surface treatments. Near the top of the maxima the surface mobility is comparable to the bulk mobility. Between these states of high mobility those of low mobility appear. A state of low order can account for considerable scattering within the minima. So far LEED has not provided any information on such multiple transitions.

Reference: E. Veuhoff and D. Kohl, J. Phys. C 14 (1981) in press.

Kinetic Equations for Physisorption

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In gas-solid systems in which the surface potential of physisorption develops many bound states one finds (Z.W. Gortel, H.J. Kreuzer and R. Teshima, Phys. Rev. B22 (1980) 5655) that the desorption kinetics are quite insensitive to details of the surface potential, allowing one to approximate a system with many discrete bound states by a quasi-continuum (for the gas particles) ranging from the bottom of the surface potential up. The adsorbing or desorbing gas particle will then perform a random walk through the quasi-continuum of bound state energies which is controlled by a (continuous) master equation which we derive from the set of rate equations for the bound state occupation functions. The kernel of the master equation is explicitly calculated for phonon-mediated adsorption and desorption in a Morse potential. We give the equivalent Smoluchowski-Chapman-Kolmogorov equation for which we find the Kramers-Moyal expansion. Identifying van Kampen's large parameter Ω for such gas-solid systems, we establish explicit criteria for the validity of a Fokker-Planck equation governing physisorption kinetics. With explicit numerical results we demonstrate that the time evolution of the adsorbate during the desorption process, as calculated from the rate equations, maintains quasi-equilibrium only at low temperatures, i.e. for $kT \ll 2U_0 / (\hbar^2 \gamma^2 / 2mU_0)^{1/2}$ [U_0 and γ^{-1} are depth and range of the surface potential and m = mass of gas particle]. Perturbation theory of the master equation yields $t_d^0 = t_d^0 \exp[Q/kT]$ with $Q = U_0$ and $t_d^0 = \omega_D^{-1} (M_s/m) (\hbar \omega_D / U_0)^4 (2mU_0 / \hbar^2 \gamma^2)^{3/2}$ at low T with ω_D = Debye frequency of solid; M_s = mass of a solid particle. At intermediate temperatures $5(U_0 \hbar^2 \gamma^2 / 2m)^{1/2} / 2 \ll kT \ll 3U_0/5$ we derive another simple expression from the Fokker-Planck equation with $t_d^0 = \omega_D^{-1} (M_s/m) 4m^2 (\hbar \omega_D)^5 (U_0 \hbar^2 \gamma^2) (*kT/72\pi)$. These results allow a critical assessment of classical "equilibrium" theories of desorption. Lower limits for the pre-exponential factor t_d^0 which can be as low as 10^{-16} secs, are derived as $t_d^0 \geq (M_s/m) (4\hbar/9\pi) (\hbar \omega_D / U_0)$ at low T and $t_d^0 \geq (M_s/m) (2\hbar/9\pi) (kT/U_0)$ in the above intermediate temperature region. The emergence of several transient time scales in gas-solid systems with many surface bound states will be demonstrated, and the usefulness of the mean first passage time assessed. Recent calculations of physisorption kinetics for multilayer coverage using a Hartree-Fock mean field approach will be presented.

TWO-DIMENSIONAL DIFFUSION VIA THE VACANCY MECHANISM - AN EXACT SOLUTION

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An exact solution has been obtained for the problem of diffusion by the vacancy mechanism in the sudden jump approximation¹. Although solutions in two dimensions have been obtained only for the square lattice, the method is easily extendable to other 2-D lattices and lattices of higher or lower dimensionality.

In diffusion via the vacancy mechanism, correlation effects complicate the motion of the diffusing atoms and reduce the rate of diffusion. Consider a monolayer of atoms on a surface where the atoms diffuse via vacancies. In order for such an atom to move, a vacancy must be positioned next to the atom. After the atom accomplishes a jump, the vacancy must move around to the front of the atom before the diffusing atom can jump again in the same direction. Hence, for the diffusing atom, all possible directions for the next jump are not equally probable.

It has long been known that the diffusion constant D differs from D_0 in absence of correlations by the so-called Bardeen-Herring correlation factor² f : $D = fD_0$. Calculations of f have been made for various lattices using analog electrical networks and the partial or complete summation of infinite series³.

Unfortunately, knowledge of the factor f is not adequate to determine diffusive behavior over short time scales (i.e. times comparable to the mean jump time). As a first approximation, the probability distribution function $P(\vec{r}, t)$ for locating a marked atom at a lattice position \vec{r} at time t was obtained from the $P(\vec{r}, t)$ in the absence of correlations by the mere insertion of the factor f . This approximation exaggerates the effect of correlations for short time scales.

Improved solutions to the problem of correlation effects over short time scales have been obtained by the approximate solution of sets of rate equations using iterative procedures^{1,5} or approximations⁴ analogous to that of Bethe-Peierls in magnetism.

We have succeeded in obtaining an exact solution to the set of equations developed by Dibar-Ure and Flinn¹ for self-diffusion in the sudden-jump approximation. The equations and their exact solutions are readily extendable to the case of impurity diffusion via vacancies. The distribution function $P(\vec{r}, t)$ is expressible in terms of integrals. Since the solution is valid for all times, it can be used to obtain the Mössbauer spectrum or other quantities which characterize the behavior over short time scales. As an added treat, the correlation factor f is expressible in terms of an integral which, in the case of the square lattice has been evaluated, yielding the (already known⁴) value of $f = (\pi - 1)^{-1}$.

¹ M.C. Dibar-Ure and P.A. Flinn, Phys. Rev. **15B**, 1261 (1977).

² J. Bardeen and C. Herring, Imperfections in Nearly Perfect Crystals, (New York; John Wiley), 1952, p.261.

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⁶ L. Gunther, J. de Physique **C6**, 15 (1976).

A Study of the Flash Desorption of CO on a Ni(111)
Single Crystal with Small Angle Boundaries (SAB)

by

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ABSTRACT

The adsorption-desorption of CO molecules on a Ni(111) single crystal surface, with small angle boundaries, has been studied using the techniques of Low Energy Electron Diffraction (LEED), Auger Electron Spectroscopy (AES), Mass Spectroscopy and flash desorption.

The crystal was exposed to CO gas molecules at pressures from 10^{-9} to 10^{-2} torr at room temperatures and 100°C . The absolute coverage of CO molecules was calculated from the flash desorption spectra. Several different desorption states were observed and activation energies for these states were calculated from the data. Possible mechanisms for each of the observed desorption states are proposed.

POSTER SESSION

F-4

RELATED TOPICS

Wednesday, August 5

15:00 - 17:00

English-Math Building Lobby

Raman Studies of O_2 on Ni(111)

E. B. Bradley, K. A. Arunkumar and J. M. Stencel

Catalytic Oxidation of SO_2 and SO_3 on Ag Powder Observed by Surface Enhanced Raman Scattering

P. B. Dorain, K. U. von Raben, R. K. Chang and B. L. Laube

Poisoning and Reactivation Studies of Tungsten Dispenser Cathodes

C. R. K. Marrian, A. Shih and G. A. Haas

Changes in the Chemical and Electronic Surface Properties During the Oxidation of Ba

G. A. Haas, A. Shih, C. R. K. Marrian and R. E. Thomas

Electrotopographic Investigations of Surface Phenomena

M. Ensanian

Raman Studies of O₂ on Ni(111)[†]

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Laser Raman spectroscopy is used to study the adsorption of O₂ on clean Ni(111). The stretching frequency (1600 cm⁻¹) of gaseous O₂ is lowered by physisorption to 1555 cm⁻¹. No frequency dependence with temperature is observed--the Raman intensity, however, increases with increasing sample temperature until the band suddenly disappears at 290°K. No Ni-O mode is observed in this temperature range. There is no evidence of O₂ being liberated into the chamber when the Raman band disappears. This result is interpreted to mean that O₂ has dissolved into the crystal surface. That the surface has reconstructed may explain Raman modes exhibited by Ni(111) above 295°K.

[†]Work supported by Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AS05-79ER10447.

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Catalytic Oxidation of SO_2 and SO_3^- on Ag Powder Observed
by Surface Enhanced Raman Scattering[†]

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Abstract

We report on the use of surface enhanced Raman scattering to detect adsorbed sulfur-oxides (SO_3^- and SO_4^-) which have been formed by catalytic oxidation of SO_2 on the oxidized Ag powder. Upon a brief exposure to SO_2 gas, the Ag powder, which was placed in an optical reactor cell under He atmosphere at 27°C, oxidized the SO_2 to SO_3^- , giving rise to two new Raman peaks at 925 and 615 cm^{-1} . These frequencies correlated well with those from SO_3^- ions of Ag_2SO_3 adsorbed on Ag electrodes and Ag hydrosols. By rapid laser heating or slow resistance coil heating (up to 108°C) of the SO_2 exposed Ag powder placed in an O_2 atmosphere, the adsorbed SO_3^- molecules are partially oxidized to adsorbed SO_4^- , resulting in a Raman peak at 962 cm^{-1} . This frequency correlated well with SO_4^- ions of Ag_2SO_4 adsorbed on Ag electrodes. Implication and extension of these sulfur-oxide results to the monitoring of kinetically significant species on Ag catalysts during reaction conditions will be presented.

[†]Supported in part by the Gas Research Institute (Basic Research Grant No. 5080-363-0319) and the Office of Naval Research (Contract No. N00014-76-C-0643).

POISONING AND REACTIVATION STUDIES
OF TUNGSTEN DISPENSER CATHODES

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ABSTRACT

The tungsten-based dispenser cathode offers a high cw current density capability resulting in its extensive use in modern microwave tubes. This type of cathode consists of a porous tungsten matrix impregnated with a mixture of barium, calcium and aluminum oxides. The matrix surface is activated by a thin film containing barium and oxygen. At cathode operating temperatures ($\sim 1450\text{K}$), the activating film is maintained by the dispensing of fresh material from the impregnant to the surface. A new requirement for some microwave tubes is a rapid turn-on (a few seconds) following a long period of dormancy (\sim one year). Whilst the tube is inactive, the residual gases in the tube vacuum ambient poison the cathode surface and may not allow the reactivation in the required time. This paper discusses the effect of various gases found in a typical vacuum tube ambient on a tungsten dispenser cathode surface. These are preliminary results from a continuing study of basic poisoning and reactivation mechanisms of various cathodes.

Commercially prepared tungsten dispenser cathodes were examined in an ultra-high vacuum system equipped with ISS, SIMS and AES for compositional information and a quadrupole mass analyzer for gas desorption studies. Work function changes were monitored using incident and emitted electrons. The cathodes were thermally reactivated following exposure to a) the ambient gases of the vacuum system and b) intentional exposure to specific gases found in a vacuum tube ambient. The results pointed to the importance of the first atomic layer in the poisoning phenomena and the greater surface sensitivity of ISS compared to AES for correlation with work function changes. Gases such as H_2 and CH_4 appear to weakly bond onto the cathode surface since they desorb at temperatures ($\sim 500\text{K}$) far lower than cathode operating temperatures. Consequently, a rapid reactivation can be achieved following adsorption of these gases. However, gases such as CO , which appear to chemisorb onto the cathode surface, start to desorb at temperatures near 1000K resulting in a slower reactivation. Thus, it appears that in an electron tube vacuum ambient the gases, which chemisorb onto the cathode surface, limit the speed of reactivation following a period of tube dormancy.

Changes in the Chemical and Electronic Surface Properties
During the Oxidation of Ba.

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ABSTRACT

The work function of an adsorbed Ba layer is strongly influenced by its state of oxidation. Since most currently used thermionic cathodes are composed of such partially oxidized Ba films, a characterization of the chemical and electronic properties during oxidation will help provide a clearer understanding of performance capabilities in modern microwave tubes. The studies reported here were on 10 atomic layer Ba films subjected to varying O_2 exposures. Chemical changes involved Auger electron and electron loss spectroscopy (AES and ELS) while recent low energy electron reflectivity (LEER) techniques⁽¹⁾ were used to determine simultaneous Fermi level and vacuum level positions with respect to the conduction band edge.

Chemical changes in passing from the metal to oxide phase were indicated by changes in the low energy Ba AES lines, particularly those in the 50-60 eV and 65-75 eV region. It was shown from XPS results that these are largely due to Ba4d-Ba5s-valence and Ba4d-Ba5p-valence transitions, respectively. The valence states are the Ba6s for the metallic phase and the O2p for the oxide phase. It was quite obvious that those AES lines involving Ba6s states all decreased with oxidation while those involving O2p states increased with oxidation. This was found to be true in the 10 AES lines that were tentatively identified. It was also noted that Ba AES lines, not involving valence states, remained relatively stable. The increased dominance of the O2p states with oxidation was also observed in the rise of the O2p ELS peak. The major AES changes were largely linear with O_2 exposure (i.e. uniform in depth) although indications were that the surface Ba layer seemed the last to be oxidized (consistent with similar results on Sr⁽²⁾).

Results of the electronic changes showed that when the Ba oxidation was nearly complete, as indicated by AES, the work function was about equal to that of randomly oriented BaO. LEER data, however, showed that additional O_2 exposure resulted in a transformation to a BaO single crystal phase whose Fermi level position suggested a high density of oxygen vacancy donors and whose large electron affinity indicated non-stoichiometry at the surface. Further O_2 exposure resulted in a BaO-type surface dipole and oxygen vacancy donor densities more typical of BaO lattices (i.e. Fermi level ~8 eV below conduction band edge). It is noteworthy that no gross changes in AES results were observed during the BaO lattice rearrangements which gave rise to the above electronic changes in semiconductor properties.

- (1) G. A. Haas, A. Shih and R. E. Thomas, Appl. Surf. Sci. 1, 59(1977).
(2) C. R. Helms and W. E. Spicer, Appl. Phys. Letters 21, 237(1972).

Electrotopographic Investigations of Surface Phenomena

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Abstract

Electrotopography (ETG) is a new procedure for the study of solids and their surfaces and is operationally based upon chemically selective, nonequilibrium, rotational contact, electrochemical potentials. It is potentially a powerful new tool for studying electronic transitions in complex multi-dimensional systems such as alloys and intermetallics, and offers a near infinite number of dimensions for test specimen characterization. In this new type of electrochemical transducer or sensor, a rolling element consists of the first electrode and the solid electrolyte, and the surface to be studied, the second electrode. A single scan consists of rolling the first electrode and the electrolyte from one end of the test surface to the other, giving rise to an analog signal or waveform. Although these voltages are volumetric in origin, surface features can clearly be delineated by appropriate filters. The procedure draws heavily upon information and communication theoretic concepts. A considerable body of previous work on solids and surfaces can now be re-examined by means of the new tool, and with particular emphasis on relaxational phenomena, chemical bonding, and phase transitions. Although under development for more than a decade, the technique is essentially unknown to the scientific and technical community at large. The unprecedented high dimensionality of electrotopography leads to the new concept of population ranking, that is, what is the rank of the test specimen or surface when measured against a large population of similar physical systems? This is in sharp contrast to much of the work done in the physical chemistry of surfaces which may be based on one or two specimens. Higher dimensionality however, can lead to conceptual difficulties, as well as to problems in cluster theory and pattern recognition. Although a body of knowledge is slowly developing which may be considered theoretical electrotopography, it presently remains, nevertheless, a comparative technique in the sense that IR spectral analysis is. ETG measurements can be made over a wide range of temperatures (-50 to 1800 deg. C) and as a function of mechanical vibrational frequencies, or combined with gas adsorption phenomena, or photochemistry etc. ETG analysis is normally considered to be a non-destructive procedure, however, special precautions may have to be taken in certain types of very thin films. With reference to the quantitative evaluation of surfaces the waveform averages can be the basis of matrices, whose eigenvalues and eigenvectors respectively, reflect the distribution of internal stored energy and genetic parameters. The author presents a brief overview, including both hardware and data analysis routines.

SESSION G

Thursday, August 6

09:00 - 11:20

English-Math 101

J. Zollweg, Chairman

Surface Molecular Dynamics of Crystallization
C. L. Cleveland, U. Landman and R. N. Barnett

Electrode-Electrolyte Interfaces
J. K. Sass

Surface Molecular Dynamics of Crystallization *

Charles L. Cleveland

Uzi Landman

Robert N. Barnett

Georgia Institute of Technology

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A new Surface Molecular Dynamics method is described and employed to investigate the epitaxial crystallization of both a normal melt and a melt supercooled to the same temperature as the substrate. The procedure allows for thermal dissipation via a dynamic bulk reservoir, thus allowing study of the approach to equilibrium. In both systems, the fluid forms layers parallel to the original surface before ordering within these layers is sequentially established. The dynamic coupling between different regions of these systems is illustrated through particle number profiles and plots by layer of temperature, potential energy, translational and orientational order parameters, and pair-correlation functions vs. time.

* Supported by DOE Contract No. EG-S-05-5489.

ELECTRODE-ELECTROLYTE INTERFACES

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Electrochemistry is currently undergoing a renaissance, primarily because of its technological importance but also because of the interesting physical phenomena which occur at the solid-liquid interface. It is increasingly apparent, moreover, that there exist very close parallels between the processes occurring at this boundary and those at the gas-solid interface. In particular, that layer of electrolyte immediately adjacent to the electrode surface can be meaningfully discussed using concepts borrowed from gas phase chemisorption.

For the benefit of those who are unfamiliar with the basic electrochemical concepts a brief review will be presented. Basically, the unique aspects in electrochemical studies arise by virtue of the ability to vary the potential drop across the interface in a well-defined manner. This galvanic potential difference results from the juxtaposition of excess electronic charge on the electrode surface and excess ionic charge of opposite polarity in the electrolyte. As a consequence large electric fields are generated which may induce pronounced structural changes in the interfacial region. In addition, the rate at which adsorbates are electrode-positated onto the electrode may be easily controlled by selecting the appropriate potential difference.

Currently a great deal of attention is being focussed on the orientation of solvent molecules in the double layer. This problem is essentially two-dimensional in nature and is related to the degree to which solvent dipoles align with the electric field at the electrode surface. Results will be presented which demonstrate the usefulness of gas phase simulation experiments for elucidating the microscopic structure of the interface.

Underpotential deposition of foreign metal adsorbates will be discussed as a particularly illustrative example of surface phase formation in an electrochemical environment. The existence of an equilibrium between the species in the solution and those adsorbed distinguishes this process from its gas phase counterpart.

POSTER SESSION H

Thursday, August 6
19:00 - 21:00
English-Math Building Lobby

W. N. Unertl, Chairman

DISCUSSION

21:00-22:00

English-Math 101

Discussion Leaders: C. L. Cleveland
P. H. Kleban
T. N. Rhodin

- H-1 Molecules on Graphite
- H-2 Physisorption Systems and 2D Melting
- H-3 Chemisorption Systems
- H-4 General Theory

POSTER SESSION

H-1

MOLECULES ON GRAPHITE

Thursday, August 6

19:00 - 21:00

English-Math Building Lobby

N. M. R. Measurements of Ethylene on Grafoil
J. Z. Larese and R. J. Rollefson

Phase Transitions in CF_4 on Graphite
P. Dutta, S. K. Sinha, J. Hastings and L. Passell

Phases and Phase Transitions of Neon Adsorbed on Grafoil
H. J. Lauter, C. Tiby and H. Wiechert

Heat Capacity Studies of Adsorbed Methane Films on Exfoliated Graphite Surfaces
A. D. Migone and M. H. W. Chan

Commensurate (2x2)-Incommensurate Phase Transition in a Monolayer of CF_4 Adsorbed on Graphite: High Resolution LEED Study
J. Suzanne and S. Calisti

Pulsed NMR Survey of CH_4 Monolayers on Graphite
J. H. Quateman and M. Bretz

Ordering of Nitrogen Molecular Axes for a Commensurate Monolayer Physisorbed on Graphite
R. D. Diehl, M. F. Toney and S. C. Fain, Jr.

A Neutron Scattering Study on the Structures and Phase Transitions of ^{36}Ar Submonolayers on Grafoil
C. Tiby and H. J. Lauter

N.M.R. MEASUREMENTS OF ETHYLENE ON GRAFOIL*

J.Z. LARESE and R.J. ROLLEFSON

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Using a pulsed nuclear magnetic resonance spectrometer operating at 24 MHz we have measured the spin lattice relaxation times (T_1) and spin echoes for ethylene films adsorbed on grafoil. Measurements have been performed for a variety of coverages ranging from 0.6 to 1.1 registered monolayers in the temperature range of 55K to 110K.

For coverages below 0.81 monolayer a single minimum in T_1 was found near 65K. In the immediate vicinity of a monolayer a single T_1 minimum was observed at 87K with a discontinuous change to longer relaxation times at 89K. For coverages between 0.81 and the registered monolayer two T_1 minima appeared. The lower temperature minimum was shifted slightly upward from the low density minimum whereas the higher temperature minimum was down shifted from the registered coverage minimum. We interpret the single minima at low coverage and at registry to be the melting of solid phases of two distinct densities. An interpretation of the two T_1 minima at the intermediate coverages will also be presented.

Limited spin echo data has also been acquired for this system which show a periodic modulation of echo envelope. The frequency of this modulation indicates that the spectrum must have a narrow width at all temperatures and coverages examined. This narrow spectrum is indicative of significant molecular reorientation.

* Supported by Research Corporation

PHASE TRANSITIONS IN CF_4 ON GRAPHITE

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and

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We will report on our ongoing studies of (a) the melting of the (2×2) commensurate phase (four-state Potts model melting); and (b) the commensurate-incommensurate transition, which is characterized in this system by a disordered 'slightly-incommensurate' phase existing over a large range of coverages and temperatures.

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PHASES AND PHASE TRANSITIONS OF NEON ADSORBED ON GRAFOIL

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With neutron diffraction the different phases of Ne adsorbed on Grafoil were identified and agree in general with the ones proposed by specific heat measurements (1). The intensity of the observed (10) Bragg-peak of the adsorbed Ne layer as a function of coverage extrapolates to zero at $x = 0.2$ ($x=1$ is the most dense monolayer) indicating that this fraction occupies strongly adsorbing sites which form no lattice.

For $T = 1.5$ K ($x > 0.2$) a lattice constant was measured which is consistent with a $(\sqrt{7} \times \sqrt{7}) R \approx 19^\circ$ structure with four atoms per unit cell in agreement with the exponential behaviour of the specific heat (1). The atoms are easily pushed out of registry by increasing the temperature $T \gtrsim 5$ K (1) or the coverage to a value higher than $x \gtrsim 0.6$.

At $T = 1.5$ K the transition from the gas solid coexistence phase to the solid phase takes place at $x = 0.92$ and the density of the densest monolayer is 0.119 \AA^{-2} (the density of the 111-plane of the 3-D solid on the sublimation curve is 0.116 \AA^{-2}). Thus the transition line is seen at a higher coverage than proposed by the specific heat data ($n \approx 0.8$). This is probably due to the fact that in the Bragg-peak is seen only the scattering of the Ne-atoms forming a lattice. Whereas all adsorbed atoms contribute to the heat capacity.

As the temperature is increased from 1.5K to 13.5K the solid in the solid-gas phase expands by nearly 2 % (the 111 plane of the 3-D solid on the sublimation curve in the same interval by 0.3 %). This is certainly connected with a rotation of the adsorbed layer with respect to the graphite (2). At 13.5 K ($0.2 < x < 0.6$) a sudden change in the line shape of the Bragg peak indicates a first order transition to a liquid-gas coexistence phase. At 16K no Bragg reflection was found manifesting the gas phase and confirming that the second series of specific heat peaks (1) near 15.5K is connected with the liquid-gas to gas transition.

For $0.6 < x < 0.9$ and $T > 13.5$ K the transition from the solid-gas phase occurs to a solid-liquid phase accompanied by a peak in the specific heat data. Whereas with increasing temperature the following transition from the solid-liquid phase to the liquid phase has not yet been seen by an event in the specific heat data. This transition is evident in the neutron diffraction measurements but it is difficult to localize it exactly. It does not agree with the proposed transition line by R.E. Rapp et al. (1). A slight compression was seen mainly when the solid has melted and the liquid was further heated similar to the behaviour of adsorbed ^3He (2).

The number of nearest neighbours was calculated for the 2-D liquid. In the liquid-gas phase the liquid seems to have only 3 nearest neighbours. This number increases to about 4.7 at $x = 0.81$ and $T=25$ K in the liquid phase.

(1) G.E. Huff and J.G. Dash, J. Low Temp. Phys. 24 (1976) 155.

see also R.E. Rapp, E.P. de Souza and E. Lerner, to be published.

(2) S. Calisti and J. Suzanne, Surf. Sci. Letters 105 (1981) L255.

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Heat Capacity Studies of Adsorbed
Methane Films on Exfoliated Graphite Surfaces

A. D. Migone and M. H. W. CHAN
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Heat capacity measurements of multilayer methane films adsorbed on Graphite Foam were made between 12 and 25 K. The heat capacity peak height and the heat of transition per molecule associated with the transition from rotationally disordered to partially ordered phases were found to decrease as the film thickness is reduced. The transition temperature was also found to shift to lower values as the film thickness was reduced.

Results of heat capacity and in situ vapor pressure measurements of submonolayer methane films on Graphite Foam will also be reported.

The heat capacity measurements were made using the a.c. calorimetric techniques.

Commensurate (2x2)-Incommensurate phase transition in a monolayer of CF₄ adsorbed on graphite : high resolution LEED study

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Sciences de Luminy, Département de Physique
Case 901 - 13288 Marseille Cédex 9, France

CF₄ adsorbed on graphite is an interesting system because it is the first up to now giving a commensurate (2x2)-incommensurate transition. This is due to the size of the molecule which is ≈ 4.61 Å in the a-b plane of bulk CF₄ to compare with 4.92 Å the nearest neighbor distance in the (2x2) phase.

We report here a high resolution LEED study of the system between 55 K and 74 K. The LEED system allows us to work with a low beam intensity ($I_e \approx 10^{-9}$ A) preventing any possible cracking of the molecules. We show that the CF₄ undergoes a commensurate (2x2)-incommensurate transition at $T \approx 69$ K in good agreement with neutron diffraction measurements /1/.

A second interesting feature of this system is a rotation of the incommensurate 2D solid as predicted by Novaco and Mc Tague /2/. This rotation starts only when the mean misfit reaches 2 %. This result agrees with Shiba's model /3/ and has already been shown for krypton /4/. The only difference is that for CF₄ the rotation starts abruptly and reaches $\approx 2.7^\circ$ for a mean misfit of ≈ 4.2 %. The value of the rotation angle is larger than predicted by N.M. or S. That might be due to anharmonic effects not included in the theories.

- /1/ H.J. Lauter, B. Croset, C. Marti, P. Thorel.
Proceedings of "Ordering in Two-Dimensions (S.K. Sinha Ed., North Holland, 1980) p. 211.
- /2/ J.P. Mc Tague, A.D. Novaco. Phys. Rev. B 19, 5299 (1979)
- /3/ H. Shiba, J. Phys. Soc. Japan, 46, 1852 (1979) and 48, 211 (1980).
- /4/ S.C. Fain Jr., M.D. Chinn, R.D. Diehl. Phys. Rev. B 21, 4170 (1980).

Pulsed NMR Survey of CH_4
Monolayers on Graphite

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Ann Arbor, MI 48109

We have measured the nuclear relaxation times T_1 and T_2 , at a frequency of 4.6 MHz, over the full submonolayer phase diagram for methane adsorbed on Grafoil. Microcomputer generated Meiboom-Gill and π , $\pi/2$, π pulse sequences are used to measure T_2 and T_1 respectively. The echo decays are signal averaged and relaxation rates determined in real time by the microcomputer. Decays, however, are also monitored visually to insure data integrity. We find rich temperature and coverage variations in our relaxation times which correlate closely with the methane submonolayer phases already mapped by neutron scattering studies^{1,2}. Our observations for these regimes are outlined below.

Registered Phase

T_1 and T_2 change exponentially as $(\text{Temp.})^{-1}$ indicative of a thermal activation process with characteristic temperature $\approx 400\text{K}$. There is no T_1 or T_2 coverage dependence in the regime.

Expanded Solid/Fluid Coexistence Region

T_1 reaches a coverage independent minimum of ~ 30 mSec while T_2 continues to rise. All T_1 and T_2 echo trains decay exp. in time rather than with two time constants as might be expected for macroscopically separated phases.

Hypercritical Fluid

T_1 decreases linearly with increasing coverage indicative of mobility changes, though T_2 is insensitive to coverage.

Compressed Solid

Decay times behave similarly to the registered solid but with a coverage dependent activation energy of 500K-800K. T_1 reaches a minimum whose temperature is coverage dependent indicating that the spin correlation time falls with increasing coverage, finally stabilizing at 1 full monolayer.

References

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2. J.P. Coulomb, M. Bienfait, and P. Thorel, Mobility Measurements of Two Kinds of Two-Dimensional Fluids: Methane Adsorbed on Graphite, J. Physique **42**, (1981) p.p. 293-306.

ORDERING OF NITROGEN MOLECULAR AXES FOR A COMMENSURATE
MONOLAYER PHYSISORBED ON GRAPHITE*

R.D. Diehl, M.F. Toney, and S.C. Fain, Jr.
Physics Department, University of Washington, Seattle, WA 98195, USA

Low-energy electron diffraction (LEED) measurements on nitrogen molecules physisorbed on the graphite basal plane have been performed. At less than one monolayer and below 47 K, N_2 forms a registered $(\sqrt{3} \times \sqrt{3})$ 30° structure on graphite(1,2). At temperatures below about 30 K, we have determined that the molecular axes orient in the plane of the graphite in a herringbone structure that produces a (2×1) superlattice of the $(\sqrt{3} \times \sqrt{3})$ 30° structure.

An indication of the molecular ordering transition was first seen in a heat capacity measurement as a small peak near 28 K for 0.6 monolayer coverage(3). A neutron diffraction experiment revealed a doubling of the unit cell for temperatures below 30 K and coverages of 0.8, 1.0, and 1.2 monolayers(4). However, the information obtained was insufficient to determine the precise structure.

In our LEED measurements, the absence of certain superlattice spots for normally incident electrons indicates a set of glide planes(5) which is consistent only with an in-plane herringbone structure with the molecular orientation predicted by the energy minimization calculation of Fuselier, Raich, and Gillis (6). Similar structures were obtained in Monte Carlo(7) and mean field(8) calculations when the crystal field was large enough to effectively constrain the molecules to lie parallel to the graphite surface.

The intensity of the $(2,1)$ superlattice peak decreases as the temperature is raised from 10 K to 35 K in a manner qualitatively consistent with the neutron diffraction study(4). We also observe that these superlattice spots become broader than the instrumental resolution at about 25 K and continue to broaden until they become too weak to see at 33 K. In this temperature range there is no change in the size of the $(\sqrt{3} \times \sqrt{3})$ 30° spots.

Theoretical arguments indicate that the order-disorder transition for the structure we observe is in the universality class of the two-dimensional Heisenberg model in the presence of face-oriented cubic anisotropy(8). This model exhibits a first-order transition in the general case(9), but a calculation specific to nitrogen on graphite is not yet available.

(*) Supported by NSF Grant DMR80-06334.

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A NEUTRON SCATTERING STUDY ON THE STRUCTURES AND PHASE
TRANSITIONS OF ^{36}Ar SUBMONOLAYERS ON GRAFOIL

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The specific heat of Ar submonolayer films adsorbed on the basal planes of graphite shows an exceptionally broad peak centered around 50 K at each coverage between $x=0.25$ and $x=0.8$ ($x=1$:= densest monolayer). The transition line at 50 K is regarded as a 2D triple line [1].

We used elastic and inelastic neutron scattering to determine the structure and the dynamics of the adsorbed phases and to cast some light on the nature of the phase transitions at coverages $0.25 < x < 0.8$ and temperatures from 1 K to 80 K.

From the observation of the (10), (11) and (20) Bragg peaks a triangular lattice structure of the Ar film, incommensurate with the substrate, is documented at all (x,T) -points investigated.

Up to 40 K the nearest neighbour distance a_{nn} is independent of coverage at constant temperature, thus proving the existence of a two-phase region between 2D solid and 2D vapour ($a_{nn}=3.87 \text{ \AA}$ at $T=1.7 \text{ K}$ and $x=0.49$ in agreement with [2]). With raising temperature a_{nn} increases similar to that of bulk Ar (0.6%). For $T < 40 \text{ K}$ the coherence length, doesn't change and the intensity is only determined by the Debye-Waller factor.

From 40 K to 60 K the intensity and the coherence length decrease smoothly, indicating a continuous change between 2D solid and 2D liquid. The thermal expansion of the film is four times that of bulk Ar in the same temperature range (3.8%). This might facilitate a continuous melting transition by adjusting the density of the 2D solid to that of a 2D liquid layer.

This result is confirmed by inelastic neutron scattering. Data taken around the zone boundary show a longitudinal mode at $\Delta E=1.36 \text{ THz}$ with a constant width from 1 K to 50 K, whereas the transverse mode ($\Delta E=0.88 \text{ THz}$) becomes damped and shifts to lower energies above 40 K. This observation can be explained by a dislocation mediated continuous melting with two characteristic temperatures T_m and T_p at 40 K and 50 K.

A first order phase transition smeared out by substrate heterogeneities appears unlikely to us, since neutron diffraction results of Ne adsorbed in the same sample cell show a sharp triple point transition over a range of 0.2 K [3].

[1] T.T. Chung, Surface Sci. 87 (1979) 348.

[2] H. Taub, K. Caneiro, J.K. Kjems, L. Passell and J.P. McTague, Phys.Rev.B 16 (1977) 4551

[3] H.J. Lauter, C. Tiby and H. Wiechert, this conference

POSTER SESSION

H-2

PHYSISORPTION SYSTEMS AND 2D MELTING

Thursday, August 6

19:00 - 21:00

English-Math Building Lobby

Density-Functional Theory of Submonolayer Phases of Kr and Ar on Graphite
D. K. Fairbent, W. F. Saam, L. M. Sander and Milton W. Cole

A Dense Two-Dimensional Gas Phase
L. W. Bruch and J. M. Phillips

The Phase Diagram of a Two-Dimensional Lennard-Jones System
J. M. Phillips and L. W. Bruch

Analysis of Orientational Order in a Two-Dimensional System Near Melting
J. A. Zollweg

Two Dimensional Melting: Behaviour of the Elastic Constants
K. J. Strandburg and G. V. Chester

Submonolayer Phases of Oxygen on Graphite
G. N. Lewis, D. D. Awschalom and S. Gregory

Finite Slope of the Specific Heat Near T_C : Substrate Effect or Triple Point
Model for 2d O_2 on Grafoil Questionable?
R. Marx and R. Hoja

Density-Functional Theory of Submonolayer
Phases of Kr and Ar on Graphite

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Abstract

A density-functional theory for two-dimensional rare gas systems adsorbed on graphite is presented. This approach allows us to go beyond a lattice-gas model and treat the substrate and interparticle interactions on an equal footing. The theory makes use of Monte-Carlo results for the pair correlation function and free energy of a uniform 2-D Lennard-Jones fluid as calculated by Henderson. We use the adatom-graphite interaction as deduced by Steele. Application to Kr on graphite produces both gas and commensurate solid phases. The phase diagram is in good overall agreement with experiment with no adjustable parameters. The liquid-gas transition of the uniform system is found to be completely suppressed due to the existence of the commensurate phase. As we use a mean-field theory, we find the gas-commensurate solid transition to be first order; however, the transition is very weakly first order where experiment indicates a continuous transition. Application to Ar on graphite produces no commensurate phase, in agreement with experiment. We believe this is the first quantitative demonstration of the absence of epitaxial ordering of Ar on graphite. We do not treat the incommensurate solid.

*Supported by the National Science Foundation

A Dense Two-Dimensional Gas Phase

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Experiments have shown that a relatively dense 2D gas may coexist with the 2D solid. Gas with density up to 15% of the 2D solid density has been observed^{1,2} for Ar, Kr, and Xe adsorbed on Ag(111). Isothermic heat data for the 2D gas support an identification of this gas as intrinsic 2D gas rather than an extrinsic gas adsorbed at "strong sites" of the surface. The dense gas has posed a severe challenge to statistical mechanical theories since in 3D the gas density at the triple point is only 0.2% of the solid density, and in 2D computer simulations for a classical Lennard-Jones potential model show³ the gas density at the 2D triple point is slightly less than 3% of the solid density. We have evaluated the equation of state of the 2D gas and solid phases for a realistic model of the adatom interactions of Xe/Ag(111), using a Monte Carlo simulation, and find that the gas density at the sublimation curve at 90 K is 14% of the solid density. The gas is highly nonideal, with large compressibility and large specific heat. The high gas density at a temperature below the triple point suggests that there is only a limited temperature range where coexistence of the gas and a 2D liquid is possible, i.e., there is only a small difference between the triple point and critical temperatures.

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3. J.M. Phillips, L.W. Bruch, and R.D. Murphy (to be published).

The Phase Diagram of a Two-Dimensional
Lennard-Jones System

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Monte Carlo simulations of two-dimensional systems of 224 Lennard-Jones (12,6) interacting particles are used to study the solid-vapor equilibrium line, the liquid-vapor equilibrium line and the melting process. Structural and thermodynamic properties are monitored for equilibrium phases above and below the melting region. Lattice dynamics provides a rigorous quantum mechanical ground state and a precise description of low temperature thermal expansion. Excellent agreement between the Monte Carlo results and cell model calculations show the cell model to be very accurate for the higher temperature region of the solid-vapor equilibrium line. A free energy construction accurately determines the melting (triple line) temperature. The melting of this small constrained system with periodic boundary conditions is first order and the latent heat is determined. Our work combined with earlier computations allow the construction of a phase diagram showing the features expected for similar systems. Graphic displays show the occurrence of dislocation pairs, voids, particle exchange, and mixed phases. The technology of simulation is discussed, i.e. the number of averaging configurations, equilibration, super heating, size effects, boundary conditions, and fluctuations.

ANALYSIS OF ORIENTATIONAL ORDER IN A
TWO-DIMENSIONAL SYSTEM NEAR MELTING

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A method is described for obtaining the autocorrelation function of the orientational order parameter field of a two-dimensional fluid simulated on a digital computer. This method, which uses Fourier transform methods, is free from the oscillations observed in correlation functions evaluated by the direct method.

A related method is also described for determining the Frank elastic constant of the system. This method has the capability of dealing with the full range of Frank constants expected -- from zero in the fluid phase to infinity in the solid phase.

These methods are applicable to a system of particles with any interaction potential. New results are presented for the hard disc system which show how these quantities behave in a system where melting does not appear to occur by the dislocation-mediated mechanism.

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Two Dimensional Melting: Behaviour of the Elastic Constants

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In a constant density Monte Carlo study of the melting of the 2-dimensional Lennard-Jones particle system we have investigated in detail the behaviour of the isothermal elastic constants over a range of densities between $\rho^* = .888$ and $\rho^* = 1.017$. Concurrently, we have studied the behaviour of the energy, pressure, average displacement of particles, and number of vacancies, along the melting curve at these densities.

In addition, we have begun quantitative studies of the behaviour of disclinations and dislocations upon passing through the melting transition.

Our results are compared with the KTHNY theory of melting in two dimensions as well as with the hypothesis of a first order transition.

The above computations were performed on a 1024 particle system with periodic boundary conditions. From 15000 to 40000 passes through the system are included in each average.

Submonolayer Phases of Oxygen on Graphite

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Recent simultaneous measurement of the specific heat and magnetic susceptibility of oxygen adsorbed on graphite indicate that the phase diagram is different to that proposed by Stephens et al.¹ in some important respects. In particular, we find firstly that the completion of the δ monolayer is accompanied by an abrupt jump in the temperature of the features thought to indicate melting rather than by a gradual shift of these features as further coverage compresses the δ phase. Secondly, and quite unexpectedly, there appears, in the coverage regime below the monolayer completion, a large feature in the specific heat. It is observed at a temperature of about 50K and has the appearance of an "upside down λ - peak". As this peak grows with increasing coverage and then suddenly vanishes just before the monolayer is completed, one must now presumably add a new phase to the phase diagram between the "melting" feature and our new feature. We speculate on the nature of this phase and its possible implications for our understanding of two-dimensional melting.

¹P. W. Stephens, P. A. Heiney, R. J. Birgeneau, P. M. Horn, J. Stoltenberg and O. E. Vilches, Phys. Rev. Letters 45, 1959 (1980).

FINITE SLOPE OF THE SPECIFIC HEAT NEAR T_c : SUBSTRATE EFFECT OR TRIPLE POINT MODEL FOR 2d O_2 ON GRAFOIL QUESTIONABLE?

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Due to largely increased accuracy of our twin calorimeter (two small copper cells filled with Grafoil disks with orientations parallel and perpendicular to axis of cells) we are now able to measure the temperature dependence of the specific heat of adsorbates very close to T_c within magnetic fields up to 5 T. The temperature resolution is $\Delta t = 3 \cdot 10^{-4}$; $\Delta t = (\Delta T - T_c)/T_c$.

We re-investigated the triple line of O_2 [1,2,3] with special emphasis on the slope near T_c of the specific heat anomalies. The new results are: a) The heights of the anomalies are infinite in principle, rounding occurs at $t_r = 10^{-3}$. The rounding is intrinsic to the studied layers and not due to finite temperature steps as was checked by applying different temperature increments. b) The slope of the specific heat near T_c is finite and symmetrical above and below T_c . c) There is no influence of magnetic fields up to 5 T neither for orientation parallel nor perpendicular to adsorption plane, indicating a pure crystalline non-magnetic phase transition.

As due to a triple point one should for infinite systems observe ideal δ -function shaped anomalies in specific heat. In experiment, however, only finite systems with grain boundaries, point defects, impurity atoms etc. are realizable. Therefore, transitions in such systems are never sharp, but spread over a temperature interval which depends on size of the system. Recently Bretz [4] investigated the 2d lattice gas-gas transition of He on ZYX and compared his findings with a former investigation of the same transition of He on Grafoil. Note that the lateral dimensions of undisturbed adsorption areas without grain boundaries etc. are in case of ZYX considerably larger than in case of Grafoil. He found for the slope of the specific heat temperature dependence for both systems nearly identical results, differences appeared in the rounding temperature t_r and in T_c . t_r was for He/Grafoil considerably larger than for He/ZYX and T_c was somewhat shifted to lower temperatures for He on Grafoil. The increased rounding temperature is close to what has been expected, since rounding of a sharp specific-heat anomaly occurs when the correlation length of the corresponding infinite system approaches the characteristic dimension of the actual system. The shifted T_c is consistent with calculations of Ferdinand and Fisher [5] for a finite 2d Ising model. In connection with our investigations, however, the most intriguing result of Bretz is that for temperatures t well above the rounding temperature t_r the slope of the anomaly is within the accuracy of measurement independent from substrate. This result is supported by the findings of Ferdinand and Fisher [5] for the 2d Ising system, which shows independently from its extension an essentially logarithmical anomaly, corrected by some higher order terms in case of finite extension. Because it is the slope which characterizes the order of a phase transition we may hope that the results based on Grafoil are equally reliable as those deduced from ZYX. Does one observe true critical behaviour of 2d systems on Grafoil? With the above deliberations in mind we may speculate upon the physical meaning of the finite slope reported above (three-state Potts-model, tricritical point?).

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POSTER SESSION

H-3

CHEMISORPTION SYSTEMS

Thursday, August 6

19:00 - 21:00

English-Math Building Lobby

The Study of a Chemisorbed Layer by Helium Atomic Beam Diffraction: Oxygen on Cu (110)
J. Lapujoulade

The Superstructures of Clean Si(111) Surfaces Upon Adsorption of Silver and Their Electronic Properties
G. Le Lay

Phase Transitions in Molecular Overlayers on Pt and Rh(111)
M. A. Van Hove, R. J. Koestner, J. Frost, P. C. Stair, L. L. Kesmodel and G. A. Somorjai

Phase Transitions of a Two-Dimensional Chemisorbed System: Hydrogen on Iron(110)
K. Christmann, R. Imbihl, R. J. Behm, G. Ertl and T. Matsushima

CO on RU(001): Formation and Dissolution of Islands of CO at Low Coverages
E. D. Williams and W. H. Weinberg

2-Dimensional Potassium Layers on Graphite: Comparison to Potassium Intercalated in Graphite
N. J. Wu and A. Ignatiev

THE STUDY OF A CHEMISORBED LAYER BY HELIUM ATOMIC BEAM DIFFRACTION :
OXYGEN ON Cu (110)

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We have studied the diffraction of an helium nozzle beam from an adsorbed layer of oxygen on Cu (110). The diffraction pattern has been recorded for oxygen coverages ranging from zero up to half-coverage which corresponds to the saturation of the (2 x 1) structure observed by LEED.

When the surface is clean only a large specular peak is present while when oxygen is adsorbed at any coverages a sharp diffraction pattern including both integer and half order peaks appear. The analysis of diffraction peaks amplitude, resonances with bound states, and Debye-Waller factors indicates that oxygen adsorption induces a reconstruction of the surface along the model proposed by de Wit and Bronckers¹ from ion scattering data. In this model in each second (100) row copper atoms are replaced by oxygen atoms.

The analysis of peak intensities at intermediate coverages supports an adsorption into islands of this reconstructed (2 x 1) structure.

1. A.C.J. de Wit, R.P.N. Bronckers
to appear in Surface Science.

THE SUPERSTRUCTURES OF CLEAN Si(111) SURFACES UPON ADSORPTION OF SILVER AND
THEIR ELECTRONIC PROPERTIES

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Abstract :

Four different superstructures, namely $\sqrt{7}\times\sqrt{7}$ -R($\pm 19^\circ$), $\sqrt{3}\times\sqrt{3}$ -R(30°), 3×1 and 6×1 are observed by LEED and RHEED /1,2,3/ in the submonolayer range in the course of silver adsorption on Si(111) depending on the initial structure of the clean substrate surface (2×1 cleavage or 7×7 annealed structure) as well as deposition and/or annealing temperatures. The coverage at completion of these superstructures is derived from Auger Electron Spectroscopy condensation/isothermal desorption curves correlated with LEED observations and $I(v)$ plots calibration of the silver incident beam and accurate determination of the sticking probability by mass spectrometry measurements. Geometrical models of these superlattices may be proposed with good confidence while the adsorption site is determined by quantum mechanical cluster calculations. It is shown for example that the $\sqrt{7}\times\sqrt{7}$ structure is completed at $\theta = 6/7$ and that the superstructure is due to an ordered array of vacancies in the ad-layer, which corresponds to a ground state of the lattice gas model.

Moreover a close correlation is established between the adsorption process and the growth mechanism of the deposit on the one hand and the electronic properties of the system recently probed using photoemission yield spectroscopy /4/, Electron Loss Spectroscopy /5/ and angle-resolved photoemission spectroscopy /6/ on the other hand.

References

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- /3/ T. Ichikawa and S. Ino, Surface Sci. 97 (1980) 489.
- /4/ D. Bolmont, P. Chen and C.A. Sebenne, J. Phys. C, to be published.
- /5/ J. Derrien, G. Le Lay and F. Salvan, J. Physique 39 (1978) 364.
- /6/ G.V. Hansson, R.Z. Bachrach, R.S. Bauer and P. Chiaradia, Phys. Rev. Lett. 46 (1981) 1033.

PHASE TRANSITIONS IN MOLECULAR OVERLAYERS ON Pt AND Rh(111)[†]

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P.C. Stair**, L.L. Kesmodel*** and G.A. Somorjai

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Abstract

C₂, C₃, and C₄ hydrocarbon molecules adsorbed on Pt and Rh(111) produce a variety of structures between which interesting phase transitions occur. Some of these transitions involve chemical changes in the adsorbed species, such as a change in the adsorption site, in the number of hydrogen atoms of the species, and in the bond order of the carbon-carbon bonds. For example, parallel bonded C₂H₂ can convert to perpendicular bonded >CCH_3 in a (2x2) arrangement in the presence of hydrogen. Also observed are order-disorder transitions involving lateral interactions between adjacent molecular adsorbates. This occurs for example with $\text{>CCH}_2\text{CH}_3$ on Rh(111) where the -CH₃ methyl groups can lock into a $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ arrangement, while the >CCH_2 -groups have a (2x2) arrangement identical to that of the >CCH_3 species.

[†] This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract W-7405-ENG-48.

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PHASE TRANSITIONS OF A TWO-DIMENSIONAL CHEMISORBED SYSTEM:
HYDROGEN ON IRON(110)

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The dissociative adsorption of hydrogen on a clean Fe(110) surface at $T = 120$ K leads to the formation of a (2x1) and, at higher coverages, to a (3x1) LEED superstructure. The diffraction intensity is apparently caused by direct scattering off the hydrogen adsorbed layer and can therefore be taken as a direct measure of the degree of order within the chemisorbed hydrogen phase. Surface contamination and electron beam effects on the hydrogen adlayer could be minimized by using a fast Video LEED technique as developed recently in the group of K.Müller [1].

For both the (2x1) and the (3x1) hydrogen phase we observe continuous order-disorder transitions as indicated by the temperature dependence of both the LEED intensity and the angular profile of the fractional order beams. The critical temperature for the (2x1) phase is $245 (\pm 5)$ K, that for the (3x1) phase is slightly higher, namely $265 (\pm 5)$ K. If the hydrogen coverage is increased beyond half a monolayer ($\theta = 1/2$) the (2x1) phase gradually transforms into a (3x1) phase (corresponding to $\theta = 2/3$) as is indicated first by a splitting of the (1,1/2) beams H in [0,1] direction and the subsequent disappearance of the (1,1/2) doublet, followed by the emerging of the (1,1/3) beams.

From the coverage dependence of the transition temperatures we derive the phase diagrams for both ordered phases which are then qualitatively interpreted in terms of the mutual interaction energies of the adsorbed hydrogen atoms.

The results are discussed and compared with recent findings on the Ni(111)/H [2] and Pd(100)/H [3] systems which exhibited less complicated phase transformations.

- [1] E.Lang, P.Heilmann, G.Hanke, K.Heinz, and K.Müller, Appl.Phys. 19, 287 (1979)
- [2] K.Christmann, R.J.Behm, G.Ertl, M.A.van Hove, and W.H.Weinberg, J.Chem.Phys. 70, 4168 (1979)
- [3] R.J.Behm, K.Christmann, and G.Ertl, Surf.Sci. 99, 320 (1980)

*) on leave from The Research Institute for Catalysis, Hokkaido University, Sapporo 060, Japan.

CO ON RU(001): FORMATION AND DISSOLUTION OF
ISLANDS OF CO AT LOW COVERAGES

by

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Upon adsorption on the basal plane of ruthenium, CO forms a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure (1-3). Results of thermal desorption (4) and infrared (5) measurements on this system indicate that there is an attractive second neighbor interaction energy between CO molecules. This should cause the CO molecules to order into islands of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure at low coverages, if the temperature is low enough.

Low energy electron diffraction (LEED) has been used to study the formation of ordered islands of CO as a function of temperature. At 100 K, the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure is observed easily at coverages as low as 1/9. (The optimum coverage for the structure is 1/3.) This confirms the prediction of island formation for this system.

The beam width and intensity have been measured as a function of temperature at coverages of 1/3, 1/6 and 0.14. At $\theta = 1/3$, there is no broadening of the profile as the temperature increases from 100 K to 400 K. There is some decrease in intensity, which is most likely due to the wagging mode of CO (6). However, at $\theta = 1/6$ and 0.14, the intensity decreases dramatically between 100 K and 400 K. In addition, the width of the profile remains constant over a range of low temperatures, and abruptly begins to increase at about 200 K for $\theta = 0.14$ and 250 K for $\theta = 1/6$.

These results indicate that disorder cannot occur within the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure below 400 K. However, the second neighbor interaction energy is weak enough to allow CO molecules to leave the ordered islands at temperatures as low as 200 K. The results are discussed in more detail in terms of a two-dimensional gas-solid equilibrium, and the value of the second neighbor interaction energy is estimated.

References

1. J. T. Grant and T. W. Haas, *Surface Sci.* 21, 76 (1970).
2. T. E. Madey and D. Menzel, *Japan J. Appl. Phys., Suppl.* 2, Pt. 2, 229 (1974).
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2-Dimensional Potassium Layers
on Graphite: Comparison to Potassium
Intercalated in Graphite

N. J. Wu and A. Ignatiev
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The 2-D character of the order-disorder phase transition of potassium intercalated in graphite has been recently much studied by x-ray diffraction. It is of interest, however, to determine the behavior of a single potassium layer on a graphite surface for comparison to the intercalate. Potassium has been evaporated from a molecular beam source onto clean cleaved natural graphite single crystals. Ordered phases have been determined by low energy electron diffraction (LEED). At low potassium exposure ($\Theta \leq \frac{1}{2}$) a 2×2 LEED pattern is observed. This is the symmetry observed for the ordered phase in the KC_8 intercalate, however, this surface phase is ordered from 80° K to $\sim 350^\circ$ K (the highest temperature for which measurements were made) in difference to the order-disorder transition at 150° K observed for potassium in the intercalate. At higher potassium exposure ($\Theta \geq \frac{1}{2}$) a $\sqrt{3} \times \sqrt{3}$ ordered phase is observed at the surface. This phase has not been observed in potassium intercalates (this would correspond to KC_6), however, this phase is observed for lithium intercalates in graphite (LiC_6). The $\sqrt{3} \times \sqrt{3}$ is ordered from 80° K to 630° K at which point the phase disorders. The details of this phase transition as well as the LEED determinations of the 2×2 and $\sqrt{3} \times \sqrt{3}$ structures are currently underway and will be also reported.

POSTER SESSION

H-4

GENERAL THEORY

Thursday, August 6

19:00 - 21:00

English-Math Building Lobby

A Theoretical Approach to Study Non-Lipidic Molecules in Lipids Mono and Bilayers: The Cholesterol Problem
A. Caillé and G. Slater

Symmetry Classification of Continuous Phase Transitions in Two Dimensions
C. Rottman

Phase Transitions in Quasi Two Dimensional Systems
S. T. Chui

The Phase Diagram of a Simple Ising Meta Magnet: 2d Square
P. H. E. Meijer and S. Ekmekci

The Role of Three-Atom Interactions in Two-Dimensional Phase Diagrams
N. C. Bartelt, T. L. Einstein and P. E. Hunter

An Investigation of the ANNNI and Asymmetric Clock Models Using Finite Size Scaling Techniques
J. M. Yeomans and M. E. Fisher

Interfacial Segregation in Multi-Component Systems
V. Kumar, S. Mukherjee and K. H. Bennemann

Electronic Theory for Surface Segregation: $\text{Cu}_x\text{Ni}_{1-x}$ Alloy
S. Mukherjee, J. L. Morán-López, V. Kumar and K. H. Bennemann

Theory of Underlayer Chemisorption
K. Shinjo, S. Ohnishi, M. Tsukada and S. Sugano

Chemisorption of CO on Mo(001)
R. V. Kasowski

Criterion for First-Order Phase Transitions
P. Kleban and C.-K. Hu

Ising Models With Random Sublattice Vacancies or Foreign Spins
C.-K. Hu and P. Kleban

A theoretical approach to study non-lipidic molecules in lipids mono and bilayers: the cholesterol problem, A. Caillé and G. Slater, département de physique, Université de Sherbrooke, Sherbrooke, Québec.

A bilayer of phospholipids forms a realistic representation of the fundamental structure of the biological membrane. Using new hypothesis, we have been able to add cholesterol to the lattice gas model of this system treated as a superposition of monomolecular layers. Under certain conditions, the spin-1 Ising model is isomorphous to the system studied. Using the mean field theory solutions of the spin-1 Ising model, we explain phase separations, the latent heat change, the suppression of the so-called pretransition, the decreasing transition temperature and increasing width observed experimentally as the concentration of cholesterol grows. Finally, using the results of two-dimensional percolation theory, the jumps in the lateral diffusion constant are explained.

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PHASE TRANSITIONS ON SURFACES. AN INTERNATIONAL CONFERENCE. ABS--ETC (U)

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DT-4

SYMMETRY CLASSIFICATION OF CONTINUOUS PHASE
TRANSITIONS IN TWO DIMENSIONS

Craig Rottman

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Extending earlier work by Domany *et al.*, this paper provides a group-theoretical classification of continuous phase transitions of systems of arbitrary $d=2$ space-group symmetry with a scalar ordering density. Based on the Lifshitz condition, the classification finds the symmetries for which continuous phase transitions are possible and identifies the corresponding universality classes according to the associated Landau-Ginzburg-Wilson Hamiltonians. Tentatively unidentified universality classes appear, associated with the space groups $p4gm$, $p3$, $p31m$ and $p6$. Applications to atomic and molecular adsorption and to surface reconstruction are given. Generalizations to "colored" space groups is also discussed.

Phase Transitions in Quasi Two Dimensional Systems by S. T. Chui,
Bartol Research Foundation of The Franklin Institute, University
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Different possible phase transitions in a stack of planes will be described. We mention here a few particular cases that are of current interest. For layers of XY spins we found a transition near $T_{KT}/2$ when the layers decouple. Then at T_{KT} a vortex unbinding transition occurs. (T_{KT} is the Kosterlitz Thouless temperature.) This may have some relevance to quasi 2D superconductivity. For melting in layers, the following sequence is possible. At very low temperature dislocations on neighboring layers interact with a potential proportional to $|r|$. Dislocations on different layers line up. As the temperature is increased the in-plane-positional long range order becomes power law like but the bond orientational order is still three dimensional. In this phase dislocations on neighboring layers interact with $1/r$ potential and does not line up. Then they can unbind. The grain boundary mechanism of melting that the author proposed recently is not applicable to this case because grain boundaries on different layers always line up. After this the bond orientational order becomes algebraic. Finally the system completely melts. This may have some relevance to recent experiments by Pindak et al. on liquid crystal films.

The Phase Diagram of a Simple
Ising Meta Magnet: 2d Square

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To obtain the global phase diagram for a 2 dimensional system with repulsive nearest neighbor and attractive next nearest neighbor interaction (meta magnet) we determined the free energy as a function of the temperature, the field and the staggered field using the cluster variation method. This was done for various ratios of the coupling parameters $\mathcal{E} = \mathcal{E}_1/\mathcal{E}_2$; $\mathcal{E}_1 > 0$ and $\mathcal{E}_2 < 0$. The three pieces of coexisting surfaces meet each other in two possible configurations: either the surfaces join in a line of first order transitions that ends in a tricritical point, or the surfaces join in a line that contains a critical end point and ends in a bicritical end point. The configuration depends on the value of \mathcal{E} .

We find that for $\mathcal{E} = -0.5$ the system has a bicritical end point, in contrast to the result of the Monte Carlo method. The point has the same reduced critical temperature. The sequence of phase diagrams as obtained with the cluster variation method has a tricritical point for values of \mathcal{E} between -0.25 and -0.3 . This differs from the molecular field result, which shows a tricritical point above -0.6 , and from the pair approximation, which shows no tricritical point at all. The renormalization group results seem always to obtain a tricritical point.

The different critical points were obtained by means of the appropriate submatrix of the hessian of the free energy.

The Role of Three-Adatom Interactions in Two-Dimensional Phase Diagrams

N. C. Bartelt,* T. L. Einstein,* and P. E. Hunter,† Department
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In most experimental phase diagrams, asymmetries are found about half-monolayer coverage. For our discussion these asymmetries can be divided into two kinds: 1) higher temperature asymmetries of a phase boundary for a long-range ordered phase with saturation coverage of $1/2$ and 2) low-temperature gross asymmetries in which some phase exists for fractional coverage θ but not for $1-\theta$. Both asymmetries are often attributed to three-adatom interactions, which break the particle-hole symmetry of the lattice-gas Hamiltonian. For the second kind of asymmetry, simple expressions for the ground state energies of the possible phases give magnitudes (or at least inequalities) for such "trio" interactions. Explicit computations for model systems produce numbers consistent with these magnitudes. These computations also show, however, that there are usually several three-adatom configurations of comparable energy, not just the one or two typically invoked to explain asymmetries.

For the first kind of asymmetry, it is not the ground state energy of the ordered state but rather the excitation energy which is relevant to determining the curve of transition temperature versus θ . Simple pictures for a $c(2 \times 2)$ overlayer on a square lattice show that the low energy excitations are symmetric about $\theta = 1/2$ when there are either linear or right-angle-triangle repulsive triads. (When both are present, the symmetry is lost.) Monte Carlo simulations verify that in these cases there is indeed very little if any high-temperature asymmetry. Mean field calculations, on the other hand, show pronounced asymmetries; this feature arises from their neglect of correlations, specifically, of the ability of adatoms to disorder near the defects in the $c(2 \times 2)$ pattern at $\theta \neq 1/2$. Generalizations to other overlayer symmetries are also discussed.

We finally discuss the square lattice gas problem with first- and second-neighbor interactions from the viewpoint that transition temperatures are intimately related to low energy excitations. The simple equation arising from this picture is a remarkably good approximation for the true transition temperature in the case of repulsive nearest neighbor and attractive second-neighbor interactions. It is better than some far more complicated schemes and resulting expressions that have appeared in the literature.

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†Also at NAVSWC, Dahlgren, VA.

AN INVESTIGATION OF THE ANNNI AND
ASYMMETRIC CLOCK MODELS USING FINITE SIZE
SCALING TECHNIQUES

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The phase diagrams of the ANNNI and three-state asymmetric clock models are investigated for $d = 2$ dimensions using finite size renormalization group techniques. It has been suggested (Ostlund 1981, Selke and Fisher 1979, Villain 1981) that both models exhibit a floating phase for $d = 2$. A discussion is given of the evidence for this resulting from our finite size scaling analysis.

The importance of recognizing the possible anisotropy of the correlation length exponent, ν , is stressed. The phase diagram of the clock model with anisotropic interactions is discussed.

Ostlund, S., 1981, to be published in Phys. Rev. B.

Selke, W. and Fisher, M.E., 1979, Phys. Rev. B20 257.

Villain, J., 1981, to be published in J. de Physique.

INTERFACIAL SEGREGATION IN MULTI-COMPONENT SYSTEMS

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We present a general formulation for studying interfacial segregation in n -component systems. The system is treated to be composed of several layers parallel to the interface. The free energy of the system is then set up using the quasi-chemical approach for regular solutions where atoms are assumed to be randomly distributed. The equilibrium chemical composition is studied as a function of bulk concentration and temperature in several layers. Both the interfacial energy and the lattice mismatch energy have been taken into consideration. The formulation can be applied to grain boundaries as well as to the surfaces of semi-infinite systems and small particles. Results are presented for some ternary alloys and compared with available experimental data.

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ELECTRONIC THEORY FOR SURFACE SEGREGATION: $\text{Cu}_x\text{Ni}_{1-x}$ ALLOY

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An electronic theory for surface segregation in transition metal alloys is presented. The system is described within the tight-binding Hartree Hamiltonian model with intra-atomic electron-electron Coulomb interaction. Both diagonal and off-diagonal disorders are taken into consideration. The internal energy of the system is calculated self-consistently using a cluster-Bethe-lattice model for the alloy. The surface composition is obtained by minimizing the total free energy under the constraint that the total number of different kinds of atoms and the number of electrons are fixed. The formulation is applied to $\text{Cu}_x\text{Ni}_{1-x}$ alloy system. The results for surface composition on (100) and (111) surfaces and its temperature dependence are presented. Good agreement is obtained with the low-energy-ion-scattering-spectroscopy data.

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Theory of Underlayer Chemisorption

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The discrete variational (DV)-X α cluster method is applied to elucidate elementary processes of chemisorption of the underlayer type forming a nitride, carbide, oxide, or fluoride layer at the Ti(0001) metal surface. Comparing the electronic structure of the Ti₆ system with that of the chemisorbed one in which, for example, a nitrogen atom sits at the body-center site of the Ti₆ cluster, we have found that a specific energy level of Ti₆ 1.6 eV below the Fermi level is found to be very sensitive to the chemisorption in agreement with photoemission data. It is pointed out that the elevation of such a specific level far above the Fermi level in the chemisorption and the subsequent filling electrons in the surface states of the Ti metal would induce a distortion of the surface lattice helping the penetration of the adsorbed atom through the first layer. The change of the electronic structure of the Ti₆A (A = C, N, O, F) system when the A atom moves from the outside to the inside of the Ti₆ cluster is also discussed in connection with the deformation process of the Ti metal surface.

Based on the results of the above-mentioned non-empirical quantitative calculation, a model Hamiltonian is constructed in order to understand systematically the underlayer chemisorption for various combinations of adatoms and metals. In the Hamiltonian the substrate part is given to the tight-binding approximation, where the hopping integrals containing metal atom coordinates are expanded in terms of deviations from the equilibrium positions. The Hamiltonian involves the electron-phonon interaction induced by the electron-redistribution on the metal surface due to the adsorption. In the strong coupling limit the Hamiltonian is simplified to Anderson's including the deformation effect of the surface lattice of the substrate.

At the first stage of studying the solution for the model Hamiltonian, a static approximation is applied and the activation energy for the adatom penetration is derived. The deformation effect is found to reduce the activation energy considerably. In this study the underlayer chemisorption is discussed in connection with the bond strength of the adatom-substrate binding, the position of the Fermi level of the metal substrate, and the electron-phonon coupling constant.

We also are attempting dynamical studies of the problem, in which non-adiabatic processes such as many-phonon excitation and radiative transitions by the chemisorption are important.

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Chemisorption of CO on Mo(001). R. V. Kasowski, Central Research and Development Department, E. I. du Pont, de Nemours and Co., Experimental Station, Wilmington, De, 19898--The extended muffin tin orbital (EMTO) energy band method has been used to perform the first ab initio self-consistent calculation of the electronic structure of CO on Mo(001) surface in a c(1x1) array. Electronic states of C and O atoms chemisorbed in a similar array have also been calculated for comparison. We find overlapping 1π and 5σ states giving rise to a 2 eV wide peak centered near 7.6 eV, as is observed experimentally with UPS. Surprisingly, no dynamic final state relaxation need be assumed for agreement between theory and experiment for this molecular state. Another peak due to the 4σ state is observed about 10.2 eV below E_F . UPS has not yet identified the position of the 4σ state. Finally, spectra calculated for C and O atoms chemisorbed on Mo give rise to structure similar to that observed with UPS for dissociated CO. Total energy calculations to determine bond sites are in progress.

RVK/dms

CRITERION FOR FIRST-ORDER PHASE TRANSITIONS*

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We present a general criterion for first-order phase transitions. Using a scaling assumption for the free energy, we show that a first order transition occurs when the appropriate susceptibility (second derivative of the free energy) diverges proportional to the volume of the system. This divergence is maximal; therefore it provides a useful way of locating first order transitions. We find good agreement with our criterion for the two dimensional Ising model.

*Supported in part by the Office of Naval Research.

ISING MODELS WITH RANDOM SUBLATTICE VACANCIES OR
FOREIGN SPINS*

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We calculate phase diagrams and other properties of spin $1/2$ nearest neighbor Ising models with random vacancies (represented by spin 1) or foreign spins (represented by spin $3/2$) with different coupling constant on a sublattice of the honeycomb (HC), square (SQ) or body-centered cubic (BCC) lattices. The HC case is exactly solvable¹, for the SQ and BCC cases we use a modified Kadanoff variational method². We find second order transitions only for $T > 0$. At $T \rightarrow 0$, the model describes³ a site percolation problem on a sublattice. We find the percolation exponent has a logarithmic correction for the HC case. For the spin problem, the transition temperature decreases linearly with vacancy or foreign spin concentration, to very good approximation, for small concentration.

¹A.N. Berker, private communication.

²Chin-Kun Hu and P. Kleban, submitted to J. Comp. Phys.

³J.W. Essam in Phase Transitions and Critical Phenomena Vol. 2,
C. Domb and M.S. Green, eds., Academic, London (1972).

*Supported in part by the Office of Naval Research.

SESSION I

Friday, August 7

09:00 - 12:40

English-Math 100

J. Suzanne, Chairman

Theory of the Commensurate Incommensurate Transition
B. I. Halperin

Restructuring and Rescaling: Adlayer Transitions in Terms of Potts
Lattice Gases, Helical Potts Models, etc.
A. N. Berker

Long-Range Interactions in Alkali Films
A. G. Naumovets

Theory of the Commensurate Incommensurate Transition

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The transition from a commensurate to an incommensurate state of an adsorbed solid layer is generally described by the appearance of a small density of domain walls, or discommensurations in the otherwise commensurate phase. Recent theoretical developments have focused on the thermodynamic role of fluctuations in the domain wall positions, and of the possible instability to melting of the slightly incommensurate phase.

Restructuring and Rescaling: Adlayer Transitions in Terms
of Potts Lattice Gases, Helical Potts Models, etc.

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Phase transitions in two-dimensional systems can be studied by successive mappings of the grand-canonical Boltzmann factor. First, a single restructuring (prefacing) transformation quantitatively maps a realistic microscopic description of the adlayer system onto a model amenable to renormalization and consistent with the symmetries of the problem. This is followed by repeated rescaling (renormalization-group) transformations. Thus, consideration of krypton and nitrogen submonolayers physisorbed on basal graphite led to the introduction of *the Potts lattice-gas model* and to the evaluation of multicritical phase diagrams with commensurate and disordered phases, in quantitative agreement with experiments. Subsequently, it is in terms of the Potts lattice-gas model that *the effective vacancy mechanism* for the changeover from second to first-order transitions was found, illustrating the feedback between direct experimental problems and more generic concepts. The study of commensurate-incommensurate transitions in oversaturated krypton layers has led to *the helical Potts model*.¹ The resulting phase diagrams show a narrow disordered region between two second-order transitions respectively to commensurate and incommensurate phases, in agreement with experiment and with an alternate theoretical approach. We find that the disordered region can pinch down to zero temperature, or terminate at a bicritical point, below which a first-order transition separates the commensurate and incommensurate phases. Similar methods are used for the chemisorption problem of oxygen, and other adsorbates, on nickel, by mapping onto *coupled Potts-Ising models*.² A variety of phase diagrams are obtained, qualitatively distinguished by tricritical points, triple points, critical end-points, and a novel bicritical point. Finally, the method of identifying two-dimensional ordering via a prefacing transformation has applications for three-dimensional anisotropic substances, e.g. giving a mechanism and phase diagrams for doubly reentrant liquid crystals, in terms of *the frustrated spin-gas model*.³

¹ M. Kardar and A. N. Berker, to be published.

² R. G. Caflisch and A. N. Berker, to be published.

³ A. N. Berker and J. S. Walker, to be published.

LONG-RANGE INTERACTIONS IN ALKALI FILMS

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This talk will be devoted to long range interactions in Alkali films and their manifestations in structural phase transitions and other film properties.

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